SCOTT BLAIR

FOODSTUFFS
THEIR
PLASTICITY
FLUIDITY AND CONSISTENCY

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Foodstuffs their.

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1. foodstuffs ② starch

3. cereals
4. rheology
5. milk products
6. butter
7. cheese
8. honey
9. food products
10. psycho rheology

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FOODSTUFFS

THEIR PLASTICITY, FLUIDITY AND CONSISTENCY

DEFORMATION AND FLOW

MONOGRAPHS ON THE RHEOLOGICAL BEHAVIOUR OF NATURAL AND SYNTHETIC PRODUCTS

EDITED BY

J. M. BURGERS
Professor of Aero- and Hydrodynamics,
Institute of Technology, Delft

J. J. HERMANS
Professor of Physical Chemistry,
University of Leiden and Groningen

G. W. SCOTT BLAIR
National Institute for Research in Dairying,
University of Reading

1953
NORTH-HOLLAND PUBLISHING COMPANY
AMSTERDAM

FOODSTUFFS
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G. W. SCOTT BLAIR
National Institute for Research in Dairying,
University of Reading

CENTRAL FOOD TECHNOLOGICAL RESEARCH INSTITUTE, * MYSORE. *
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1953
NORTH-HOLLAND PUBLISHING COMPANY
AMSTERDAM

Sole distributors for U.S.A.:
Interscience Publishers, Inc., New York

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PRINTED IN THE NETHERLANDS

INTRODUCTION

That "The Rheology of Foodstuffs" should form the subject matter of one of the Monographs on the Rheological Behaviour of Natural and Synthetic Products would seem to follow from the community of interest which undoubtedly exists between those working in the various food industries.

By comparison with most of the other volumes in this series, however, the present book describes work at a comparatively early stage in scientific development. The fundamental aims of rheology are to study the relationships between stress and strain systems and their time derivatives. Frequently, but by no means invariably, this is best done in terms of molecular models. These sometimes have no more than a symbolic significance: in other cases they throw light on existing molecular configurations.

The study of the rheology of foodstuffs is still almost entirely at the empirical stage of development. Such models as have been proposed are generally no more than visual aids to the understanding of empirical equations. The springs and dash-pots used to depict the behaviour of flour doughs, for example, cannot directly represent any simple structure of protein chains operating within a viscous matrix of starch paste. In so far as it is possible to express the behaviour of doughs in terms of a small number of relaxation times, with their corresponding viscosities and elastic moduli, the resulting exponential equations can be envisaged by means of pictures of springs and dashpots or, equally well, of condensors and resistances. But we know practically nothing about what is really happening at the molecular level.

The rheological behaviour of the various foodstuffs is important for very varied reasons. In some cases, the main interest lies in that little-studied Gestalt, "Masticability", which undoubtedly depends on chemical as well as on physical factors. It has been alleged that apples, grown on soil treated with different artificial fertilizers, develop skins which are, in some cases, unpleasantly tough; but the writer has been able to find no significant correlation between subjective assessments of "toughness" and the tensile strength or ductility of the skins (unpublished work).

In other cases, such as that of junket, rheological properties are said to be related to digestibility (see Chap. III). Here again, since digestibility is very hard to measure accurately, correlations are difficult to establish. Or it may be that unsuitable rheological states prevent desirable microbiological development, as with cheese (Chap. V), or make the foodstuff difficult to handle, as with butter (Chap. IV). The properties of an intermediate product such as flour dough (Chap. II) largely control subsequent processes of manufacture and hence the quality of the finished product.

In all these cases and in many others, the criterion of quality which defines optimum rheological conditions must be the subjective assessments made by manufacturers, judges or consumers.

This emphasis on subjective quality necessitates a psycho-physical approach (Chap. VIII) not only as a temporary expedient, until such time as a more fundamental understanding of molecular conditions has been reached, but as an entirely legitimate and exceedingly interesting permanent research tool capable of giving valuable basic information in its own field.

The use of empirical physical tests which do not measure properties invariant to changes in experimental technique, is widespread in the food industries. The rheologist cannot ignore this fact and, if he regards the industrial testing laboratory as little better than "a vale of misery", he can at least "use it for a well". Statistical studies from such accumulations of data have their own interest and, although the techniques available still leave much to be desired, this type of investigation has the advantages that statistical factors can be isolated which show a real measure of stability in cases when no simple physical properties can be found. Moreover, subjective quality scores and empirical rheological test data, since they are all expressed in terms of standard deviations, can be directly compared without dimensional inhomogeneity.

The expert or consumer classifies materials existentially: certain individual samples behave to a greater or a lesser extent in the same sort of way. The behaviour is not defined in terms of ideal systems. No one seriously worries about the properties of a perfectly masticable or digestible material: the definition of flour strength or cheese body does not postulate the perfect flour or the perfect cheese even in a nominalist sense.

A concept is derived, not from a precise connotation of simple behaviour but from the empirical observation that certain materials have something in common. It is alien to the expert's craft to attempt to express this "something" in quantitative terms. The best that can usually be done is to persuade him to describe each individual sample as "very good, good, average, poor or very bad" and then afterwards to score these categories from 1—5 in accordance with what Stevens has called an "interval scale" (Science, **103**, 677, 1946). This process introduces quantity into an existential situation in a way which may be criticized on philosophical grounds but, for the present at least, it would seem to be justified pragmatically.

The physicist's approach, on the other hand, is essentialist. "Forms" such as those of the Newtonian fluid and the Hookean solid and many other "bodies" well-known to rheologists, are too valuable to lose. Perhaps the greatest problem which the foodstuffs rheologist has to face is that of trying to coordinate these two disparate viewpoints.

He is not alone: if he can gain comfort from the struggles of fellow workers facing almost identical problems in another field, let him read H. J. Eysenck's recent book *The Scientific Study of Personality* (London, 1952) in which the author draws interesting parallels between stresses and strains in the human personality, (together with the causes of its breakdowns) and recent theories concerning the failure of metals.

The method of "criterioanalysis" proposed by Eysenck, which cannot be described in detail here, may well prove applicable to rheological problems in the food industries. Orthogonal factors can be derived from matrices of correlation coefficients between batteries of empirical tests, but the first of these factors need not coincide with the centre of gravity of the test vectors (see Chap. VIII). The whole system of coordinates may be rotated to conform to the criterion of some subjective standard.

What is the nature of these standards? One suspects that in many cases they are highly artificial and that they have been developed by random, or extraneous psychological processes. One has only to observe the unaccountable changes in fashion at dog shows or mannequin parades to suspect, by analogy, that many of the requirements of prize-winning foodstuffs bear little relation to nutrition or even to public taste, though it must not be forgotten that the latter can be trained to suit the trade as easily as it can be educated to appreciate scientific values.

The industrial rheologist, however, must relate his measurements to the expressed requirements of the trade whatever he may personally feel about the objectivity of these requirements. He may hope, nevertheless, by collecting scientific information, gradually to influence the directors of his industry to appreciate better the possibilities of scientific method in helping them to define their standards.

The Editor has found some difficulty in defining the limits of the subject matter of this book. Clearly there must be some overlapping with materials used for purposes other than food. Especially is this true of work on starch (Chap. I). The authors of this chapter could not have ignored altogether the many uses of their material outside the food industry, even though they may have trespassed to a small extent into a field covered by another volume in this series. Starch is also an important constituent of flour: the authors of Chapters I and II have therefore been careful to coordinate their work as far as possible.

The whole of this book is written in English, though about half the authors are from Holland. The Editor cannot but express his profound admiration for the facility with which his Dutch colleagues write in a foreign tongue. In accordance with the general editorial policy for these Monographs, no attempt has been made to prepare the text precisely in the style of an English-born writer: the only alterations in the original texts have been in those places where there might have been misunderstanding, or difficulties for the reader.

The English language is spoken in many parts of the world and there are words which are spelt differently in different continents, and others whose meanings differ locally. Even within a single country, the technician and the man in the street sometimes use the same word in different senses. The convention throughout this book has been to use spellings current in England and to explain, wherever necessary terms about which any misunderstanding is possible. A few special remarks should be made, however.

In Chapter II the words "cookie", "biscuit", "cracker" and "crumb" have very different meanings in different localities. The term "cookie" is seldom used in England (as distinct from Scotland) but has been kept in the text when quoting American work. The Shorter Oxford Dictionary defines this: "In U.S., a small cake with, or locally without, sweetening". The same authority gives for "biscuit": "A kind of crisp dry bread, more or less hard, made generally in thin flat cakes. The essential ingredients are flour and water or milk, without leaven [yeast]. In U.S., a soft cake, usually fermented". (It is right to add, however, that many American biscuits are made with baking powder and not yeast). Referring to English work, the term "biscuit" is to be taken in the former sense and is approximately equivalent to the American "cracker". ("A thin hard biscuit". O.D.).

The word "crumb" also requires a little explanation. In ordinary English parlance, a "crumb" is a very small piece of bread or cake formed by "crumbling" the material, say, between the fingers. But technically, "crumb" generally refers to "crumb-structure": i.e., the texture of the material not necessarily following crumbling. It is hoped that readers, European, American; technical or lay, will find no confusion in these definitions.

Likewise, in Chapter VII, the term "sweets", as used in England, corresponds approximately to the American "candies".

Chapters I—V refer to work on materials each of which forms the basis of a large-scale industry. Few other foodstuffs have, individually, been the subject of any appreciable body of rheological research. It has been difficult to decide how to deal with the important but isolated experiments which have been done on other materials.

The British Food Manufacturing Industries Research Association has carried out experiments on a variety of foodstuffs over many years and, in most cases, the results have been published only in privately circulated bulletins. Mr. H. G. Harvey has summarized much of this work in Chapter VII and has also discussed such other researches on miscellaneous materials as seemed worthy of mention. We are indebted to the Director and Council of the Research Association for this collaboration.

The publication of the book has been unavoidably delayed. A few of the chapters were written two or three years ago. This delay, originally resulting from the indisposition of the editor, had to be prolonged because of the serious illness of one of the contributors, Dr. Hintzer.

The editor, in expressing his thanks to all his collaborators, would wish to make special mention of Dr. Hintzer, who, while his activities were still much restricted on medical grounds, gave so generously of his limited time and strength to complete his contribution and so to prevent further delay. It is good to hear that his health continues to improve.

Many years ago, Professor W. D. Bancroft gave a lecture to his students (including the writer) at Cornell University on "Ripening the time". He pointed out that two processes are required before scientific research can be usefully applied. The first is investigation itself and the second is to prepare the way for its application. This is perhaps most clearly seen in the plastics industry. Look up almost any group of high polymers in a standard textbook and you will find something like this: "X noticed, as far back as 18—, that if the monomer M is heated with a little hydrochloric acid (perhaps containing mercury from a broken thermometer, or ash from a cigarette) an impure resinous solid compound is formed. But it was not until 19— that Y investigated this substance and found it to be ideal for making buttons, telephone receivers or dentures."

The editor suspects that many rheological discoveries, now relegated to library shelves, will, when the time is ripe, be usefully applied through industry, to the betterment of society. It is the purpose of this series of Monographs to hasten the ripening of the time.

G. W. SCOTT BLAIR

Reading, England, August 26th, 1952.

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CHAPTER I

STARCH

BY

J. HOFSTEE AND A. H. A. DE WILLIGEN
(EXP. STA. FOR POTATO PROCESSING, GRONINGEN, NETHERLANDS)

0. Introduction

Starch as an industrial raw material is a biological entity (BADENHUIZEN [1949]) more or less subjected to alterations of chemical and biochemical character during its formation and processing. Its chemical properties have been elucidated in recent years to a rather satisfactory extent, and two main components are assumed to exist, viz. amylose, with unbranched chains of glucose units, and amylopectin, a branched polymer. Even more important is its crystallographic structure. It shows a more or less distinct X-ray spectrum (KATZ [1930b]), which is gradually disturbed in pasting.

Almost the whole quantity of starch used for industrial purposes is pasted with water. This operation is not merely a dissolution to form a homogeneous liquid. In most cases the original structure of the grain is only partly disorganized (CAESAR [1944]), so that the remains of the starch particle form a discontinuous phase (GALLAY [1936]) embedded in a liquid, which itself varies from practically pure water to a really concentrated starch solution.

For the evaluation of starch and starch products three aspects of starch rheology are of paramount importance:

(1) The alterations of the rheological properties during pasting.

(2) The hot paste viscosity and its variations with time.

(3) The change in rheological properties during and after cooling of the pastes (cold paste viscosity, jelly strength).

In 2. 2, there will be ample opportunity to describe the influence of the chemical composition on the paste properties. But—in our judgment —precedence has to be given to the grain structure with the consequent important applications in which the structure is more or less retained. In all these cases the properties of the pastes are governed in a conclusive way by the method in which pasting or cooking is done. Our description therefore begins with a concise description of the pasting and swelling in hot water.

1. Potato Starch

1. 1. *Pasting*

Because the authors are working mainly with potato starch, the present paragraph is restricted to this topic. In the opinion of the authors much of the experimental data with potato starch might be relevant to other starches as well, because the differences are often gradual rather than fundamental.

On heating with water a series of changes occur, the most important being:

Increase in conductivity (DEDEK, JELINEK & KULCIKY [1936]).

Loss of birefringence (VAN ITALLIE [1930]).

Change in translucence (KÜNTZEL & DOEHNER [1949]; MORGAN [1940]).

Change in X-ray diagram (VAN ITALLIE [1930]).

Swelling of the grain (VAN ITALLIE [1930]).

Abrupt increase in viscosity (MULLEN & PACSU [1942]).

These phenomena occur within rather a small interval of temperature, which is conventionally called the gelatinization point.

These changes however do not occur at the same time, and certainly not at a sharply defined temperature. For example at a certain temperature the birefringence often disappears in one part of a grain only, the other part still showing optical activity (BEAR & SAMSA [1943]).

A sample of starch is always a collection of botanical individuals of varying diameter and shape. The single particles are not transformed at the same time, or at the same temperature. The transition temperatures are spread according to statistical laws. Some of the smaller grains keep their optical anisotropy even after prolonged heating above 60° C. Usually there is a definite negative correlation between the diameter of the particle and the transition temperature (KATZ [1933, 1934b, 1937, 1938]).

This initial stage is not so important from a rheological point of view. The viscosity of the raw starch slurry itself does not vary by more than a few percent. The rheologist's interest starts at the point where the starch grains have been swollen to such an extent, that the consequent increase in viscosity becomes evident.

On further heating, the grains continue to swell, but at an accelerated pace. There is a great deal of speculation about this phenomenon especially in the older literature, which is uninteresting from a rheological point of view. A thorough study of this swelling mechanism has been made by BEAR & SAMSA [1943]. It is concluded that the swollen grain does not burst, as is often suggested, but rather collapses at the end of the swelling period. Folds and wrinkles are formed (Fig. 4).

This swelling is accompanied by an increase in viscosity. At least in the initial stage this depends only on the swollen grains themselves and not on an increase in viscosity of the interstitial liquid. This liquid can be separated by centrifuging and turns out to be almost free of starch. Although — even in an advanced state of swelling — it is possible to separate the individual swollen starch grains, there might be an interaction, if not a sticking together of the swollen grains at higher concentrations (5—10 %).

Some authors (e.g. WIEGEL [1936]) take it for granted that the increase in viscosity at this stage is a simple function of the enlarged volume of the particles. The relation therefore might be written in the form of the Einstein equation. But the constant is not 2.5. BRIMHALL & HIXON [1941] claim to have obtained a linear relationship at small concentrations. RIPPERTON [1931], MEYER & FULD [1942] however do not find a linear relationship of the swollen grains and the viscosity of the paste. The deviation might have its origin in the way in which the particle volume is determined. RIPPERTON [1931] and VAN ITALLIE [1930] use a spontaneous settling of the grains, BRIMHALL & HIXON [1941] determine the volume after centrifuging.

GALLAY [1936] made an attempt to obtain a linear function by introducing the factor "effective volume" for the volume term in the Einstein equation. This is the reciprocal value of the "critical concentration", the maximal concentration at which the paste shows laminar flow and obeys the Hagen-Poiseuille law. Each starch sample however has its own critical concentration and so in this way a comparison of different samples is given rather than a general relation between viscosity and swelling.

Instead of a linear relation RIPPERTON [1931] obtained a proportionality between log viscosity and swelling at different starch concentrations. This relationship however was not the same for different samples. This might indicate that besides the swelling (as measured by the sedimentation volume) there must be at least one other factor influencing viscosity.

> Brimhall & Hixon [1941] also found no linear relationship at moderate concentrations. Moreover curves of pastes of one definite sample observed at different temperatures did not coincide. This again indicates that the volume of the swollen grain is not the only factor governing the viscosity of the paste.

In the studies mentioned above the temperature was kept constant. It is more important to study the influence of increasing temperature on a paste of constant concentration. Samec [1927] and van Itallie [1930] found a rapid increase of swelling with rising temperature. The same holds for the viscosity. In this case very little is known about the numerical relationship of swelling and viscosity.

At a still higher temperature, or after prolonged heating, the coherence of the swollen granule is broken down. At this stage the influence of the unavoidable stirring plays an important role and promotes the gradual dissolution. Meanwhile for some grains this destruction does not occur. As in the first stage, some individuals escape disintegration for hours. The tearing of the vesicles results in a decrease of the viscosity which is only partly compensated for by the increase of the viscosity of the interstitial liquid.

In potato starch pastes it is very difficult to destroy the last traces of micellar organisation (Caesar [1944]). In industrial practice this is hardly ever accomplished.

1. 2. *The Viscogram and its Interpretation*

The sequence of phenomena mentioned in the foregoing section dictates the alterations in rheological properties during pasting. In view of what has been said about the complex nature of the pasting process it will be clear that a thorough study is possible only when the heating is performed under rigid standardization of all factors concerned and with continuous recording of the changes. A series of instruments has been designed to meet these requirements. We mention the Brabender Amylograph (Anker & Geddes [1944]), the Brabender Viscograph (Pagenstedt [1951]), the Corn Industries Recording Viscometer (Kesler & Bechtel [1947]), the V.I. Viscograph (Selling & van Lamoen [1947]).

The instruments mentioned work on the same general principle (Fig. 2). A mixture of starch and water is put into a beaker, in which a stirrer of special design is placed, coupled to a synchronous drive. The mixture is heated in a reproducible way, by an electric heater or in an electrically heated water bath. The rate of heating can be controlled. Heat is supplied until a fixed end temperature is reached e g. the boiling point. From this point on, the paste is kept at a constant temperature for a certain time (e.g. comparable with the storage period in industrial use). Often it is possible to study the viscosity during a succeeding cooling period.

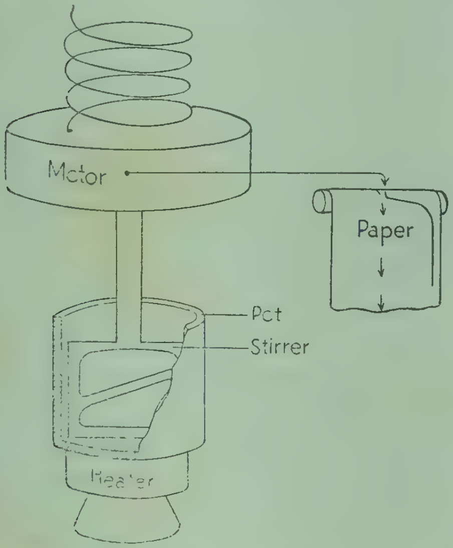

FIG. 2. Schematic drawing of the V. I. viscograph.

The torque of the stirring rod is registered by a dynamometer, so that a curve is obtained in which viscosity is plotted against time of heating.

The following variations of the cooking conditions are allowed for: viz. the rate of heating, the paste concentration (up to the maximum that can be handled by the instrument), the rate of stirring and the range of the dynamometer.

In Fig. 3 are given some examples of viscograph curves. Fig. 3a is a V.I.-viscograph record of a potato starch paste of 8 %. Fig. 3b is a curve from the Corn Industries Recording viscometer for the same starch at 8 % concentration. Fig. 3c is a Brabender amylogram for another starch sample, in 5 % paste.

The interpretation of such a viscogram is not easy. As discussed in § 1. 1 the viscosity in the swelling stage cannot be calculated in the terms of the Einstein equation, even in very dilute pastes, because the particles are not rigid. Moreover the volume ratio between the dispersed and the continuous phase is too large (at least in industrially used concentrations) for the Einstein equation to be valid. Even after prolonged cooking the Hagen–Poiseuille law does not hold (GEINITZ

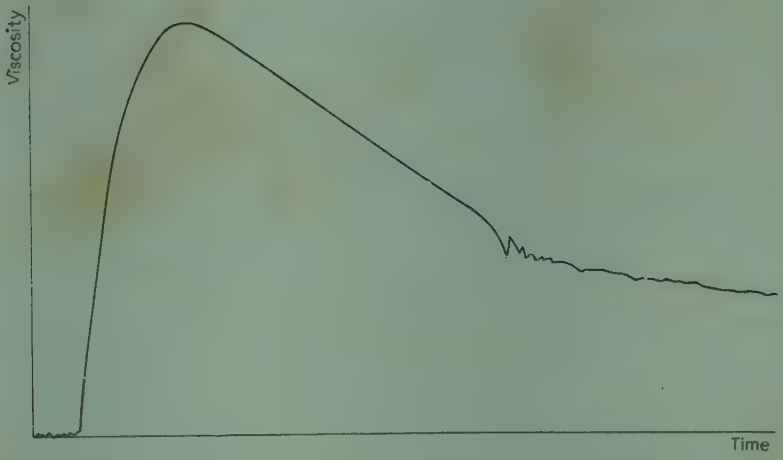

FIG. 3*a*. V. I. viscogram of 8 % potato starch paste;

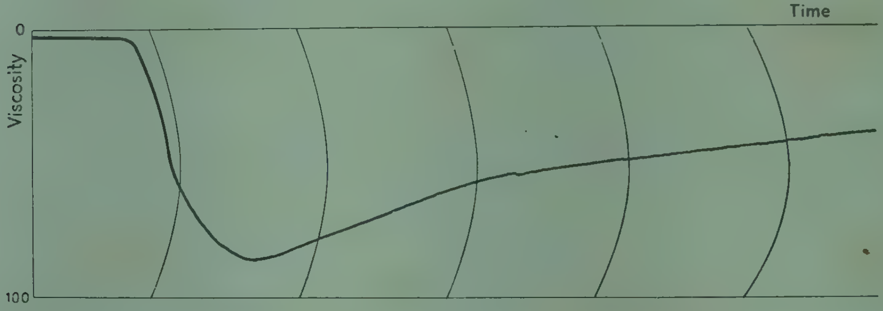

Fig. 3*b*. C. I. viscogram of 8, 10, 11 and 12 % potato starch paste;

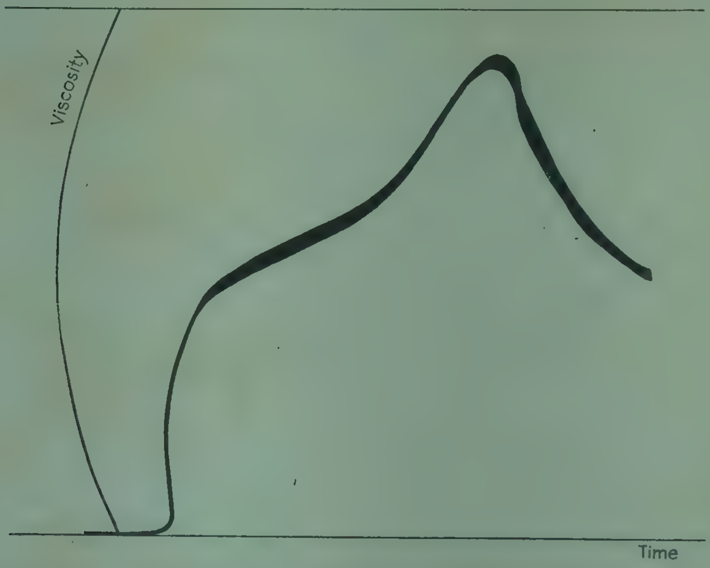

Fig. 3*c*. Brabender amylogram of 5 % potato starch.

[1940]). The viscosity is dependent on the acting shearing stress and consequently on the conditions of measurement of the specific instrument. For the purpose of normalization the designers recommend a calibration with Newtonian liquids of suitable viscosity e.g. oils.

By the use of microphotographs (Fig. 4) taken at characteristic points of the viscograph curve an insight can be obtained into the rheological variations. A certain percentage of the grains has swollen to a quite big volume before any changes in the viscosity are registered. However, at the moment where the major part of the granules begins to swell, the viscosity rises in a very rapid way up to the point where the first tearing of the swollen grains becomes noticeable. From this point on, the viscosity decreases steadily, and in concentrated pastes (from 6—8 % up, the ordinary concentrations for industrial use) the hot paste viscosity is still influenced by undissolved granules and granule fragments even after cooking for some hours.

The microphotographs give several good examples of the elongation of the granules by the action of the stirrer. In the later stages of cooking the action of the stirrer is of major importance. Up to 50 % of the viscosity of the cooked paste can be destroyed by it. In industrial use the same holds for any mechanical action such as pumping, forcing through a small opening (e.g. an expansion valve in a pumping system), or by passing the paste between glue rolls.

It can be shown that the shape of the viscogram is strongly dependent on the rate of hydration during swelling. When the uptake of water is hampered by adding substances like glycerol, quite different curves are obtained. A set of curves at increasing glycerol concentrations is shown in figure 5. A glycerol concentration as small as 10 % is sufficient to

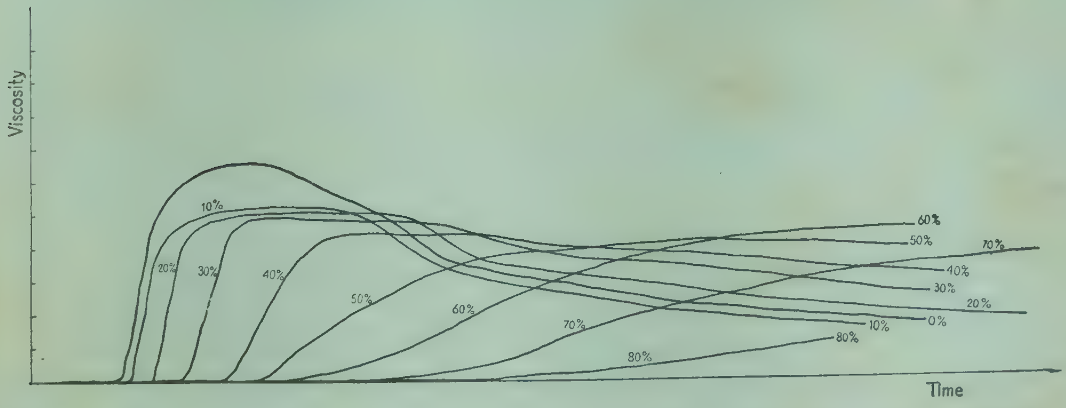

FIG. 5. Viscograms of 8 % potato starch pastes made up with different glycerol concentrations.

flatten the maximum of the curve. Considering the fact that the viscosity of the dispersing liquid is increased rather than decreased by glycerol, this is additional proof that the viscosity of the paste hardly depends on the viscosity of the interstitial liquid. At higher glycerol concentrations the point of sudden increase in viscosity shifts to higher temperatures, and the descending part of the curves disappears.

For a better discussion of the viscograms we may characterize their shape by certain data. Some point on the flat part of the curve is chosen as an arbitrary zero time (e.g. the point at which 50° C is reached). From this time on we note the following characteristic data:

The time (temperature) at which the first rise in viscosity is recorded.
The slope of the curve in the first minute after this rise.
The maximal viscosity.
The time at which this maximum is obtained.
The viscosity after prolonged heating (at least 10 minutes after reaching constant temperature).

Generally speaking, the reproducibility of these data taken from records of the instruments mentioned is very good. Reproducibility within 2 % using one single instrument is claimed by SELLING & VAN LAMOEN [1947]. In our experience it is somewhat more difficult to get a comparable agreement between different instruments of the same type. Especially with the spring dynamometers of the V.I. viscograph it is difficult to obtain exactly the same readings from different instruments.

It might be of advantage to give some practical hints about the usefulness of the three types of instrument.

The Corn Industries Recording Viscometer is of rather heavy construction. It is designed for corn starch[1] and can therefore handle potato starch pastes of relatively small consistency only. The authors adapted it to pastes of higher concentration and higher viscosity by minor changes. A disadvantage is the large volume of the sample beaker (1000 ml) which requires a sample of about 100 g dry starch. The construction allows for varying the rate of stirring. The dynamometer has three velocity ranges. The chart velocity can be changed in a proportion of about 1 : 100. A thermoregulator is attached to the water bath.

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[1] Commonly known in England as "Cornflour".

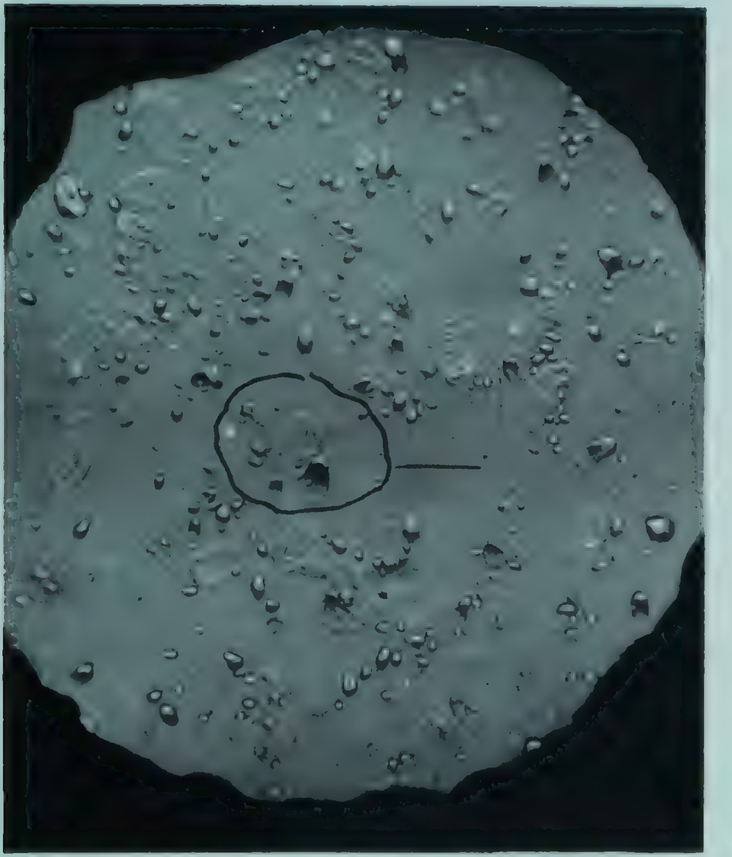

Fig. 1. Potato starch pasted at 59° C. Framed area showing a grain without any birefringence, three grains with a small area of unchanged structure and several small unpasted particles (microphotograph J. C. de Man).

Fig. 4a

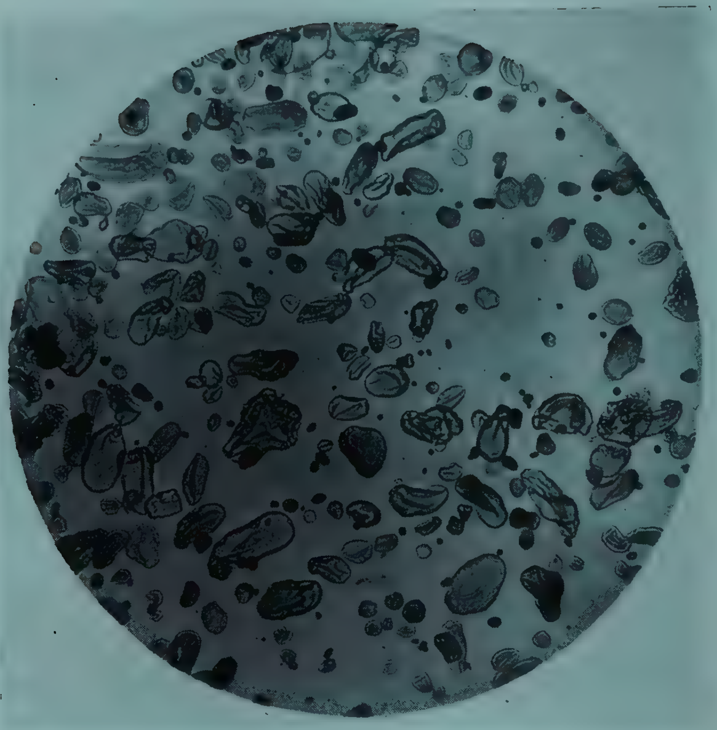

Fig. 4b.

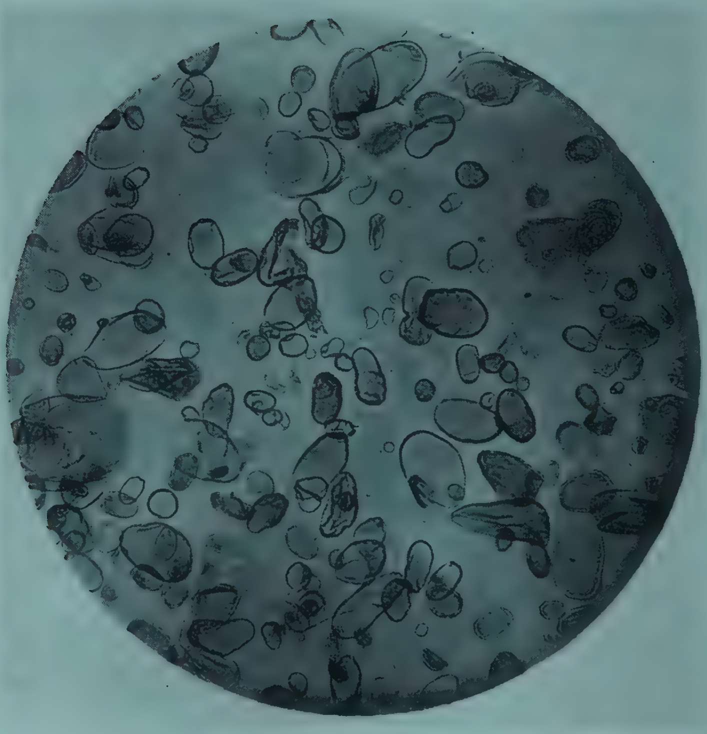

Fig. 4c

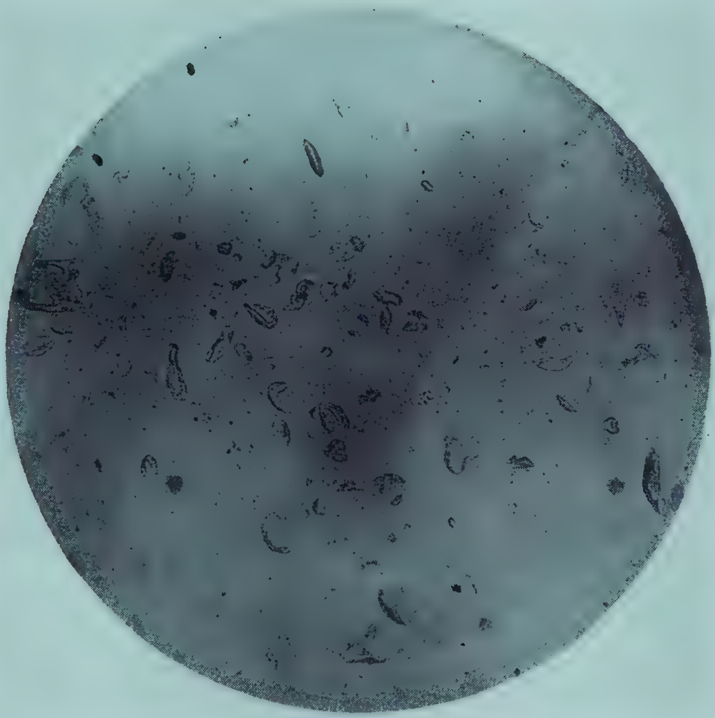

Fig. 4. Microphotographs of starch particles in samples taken from the Corn Industries Recording Viscometer in the course of the pasting process (microphotographs J. C. de Man). a: partly pasted (before the rise in viscosity has taken place), b: at the maximum of the curve, c: after heating for one hour.

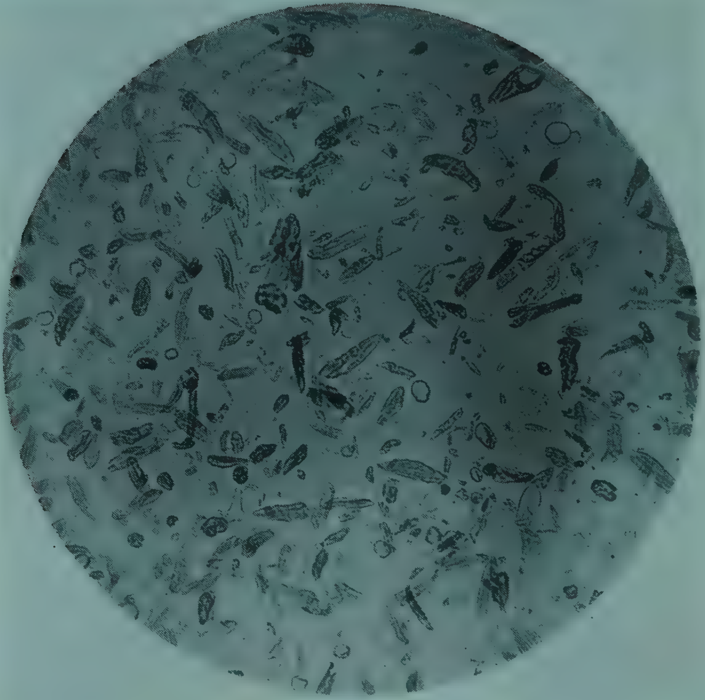

FIG. 16. Heat-moisture treated starch after heating and stirring for one hour in the Corn Industries Recording Viscometer. The conditions are exactly the same as those of the last stage in figure 4. (Microphotographs J. C. de Man).

The V.I. Viscograph is of simpler construction and much cheaper. It can handle pastes of high consistency (potato starch up to 10 %, corn starch up to 15 %). But it is not easy to adapt it to lower concentrations. Some distinct disadvantages compared with the C.I. Viscometer are: it is difficult to determine the exact temperature of the paste; no provision is made for condensation of evaporating water, and in consequence a rise in concentration might occur after prolonged cooking, no provision is made for keeping the temperature at an arbitrary point.

Nevertheless the instrument is very useful for most practical purposes. In the textile and cartonnage industry, where 10 % potato starch pastes are used, it is the only instrument which can predict the behaviour of a starch for factory purposes.

The Brabender Amylograph has been designed for use with wheat starch and flours. These materials do not pass through a stage of rapid change in viscosity like potato starch, and do not require so much stirring (wheat starch has smaller grains). In concentrated potato and corn starch the pins of the stirrer tend to form a hole in the material, and overheating of the unstirred part cannot always been avoided. Nevertheless, to the user who is aware of the limits of its possibilities this instrument is as efficient as the other apparatus.

The Brabender Viscograph is more strongly built than the Amylograph and has a different type of stirrer.

The general shape of the viscogram has proved to be of value not only for a prediction of the cooking process. For many purposes a high peak in the curve is desirable, even in those cases where the paste has to undergo a prolonged heating before use. A high peak can be an indication of the ease with which the granules can be desintegrated. Properties like "length", viscosity of the cold paste, jelly strength, are often correlated with this peak viscosity. To the technical user the viscograph curve makes possible the prediction of such properties in advance and without delay.

On the other hand we urge caution against a too easy interpretation of the viscograph curve in terms of industrial use. The pastes are too intensively stirred in this instrument and particles will be much more broken down than by batchwise pasting on a factory scale, where heating is usually done with open steam. This applies especially to jelly studies, where the paste is cooled with the stirrer of the viscograph turning (KESLER & BECHTEL [1947]).

1. 3. *The Influence of Starch Concentration*

To give an insight into the influence of the concentration on the behaviour of a starch paste in the viscograph, we will discuss an example (HOFSTEE [1950]), in which a good quality of potato starch was used. Fig. 6 shows some viscograms for different concentrations. It is clearly seen that an appreciable alteration in the shape of the viscogram occurs. The most striking points are:

> The peak height of the curve decreases with decreasing concentration.
>
> At lower concentrations this maximum is reached at a higher temperature.
>
> At intermediate concentrations (about 6 %) the ascending part of the curve shows a point of inflection. This might be an indication that the swelling process, which causes the rise in viscosity, occurs in two separate stages.
>
> At very low concentrations the difference between "maximum viscosity" and "end viscosity" disappears.

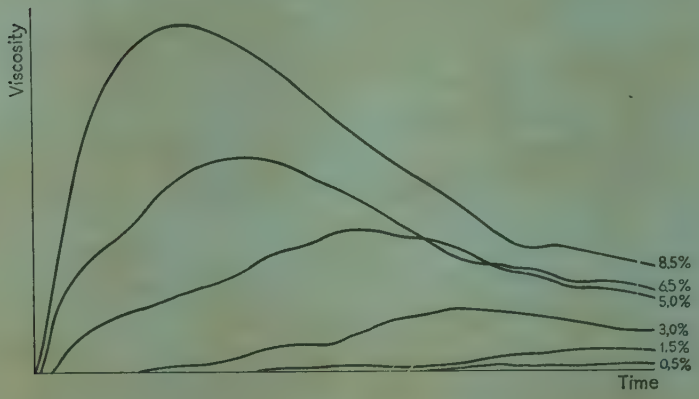

FIG. 6. Viscograms of potato starch at different concentrations (HOFSTEE [1950]).

The difference in form of the curves can be discussed at least qualitatively by the study of microphotographs.

> In 2 % starch slurries the grains swell to their maximum volume before any change in viscosity is registrated. At more elevated temperatures an increased viscosity is observed, although no marked enlargement of the particles is noticeable. But some grains assume a stretched form. At still higher temperatures the contours of the grains gradually disappear, until only small fractions are left.
>
> In the 4 % paste the maximum volume of the particle is reached after an increase in viscosity becomes noticeable. From this it may be concluded that the increase of the volume of the grains plays a part in building up the measured viscosity.
>
> In the 8 % paste many of the swollen grains are ruptured at the same time at which maximum swelling occurs. According to

> Katz the occurrence of the maximum in the curve coincides with the rupturing of the granules.
>
> It is easy to understand now why the maximum of the recorded curve is shifted to the left at higher concentrations. The higher the concentration, the higher the shearing forces and the sooner the limit of extensibility of the grain will be reached, when rupturing will occur.

It is shown by BECHTEL [1947] and ANKER & GEDDES [1944] that there is a linear relation between the logarithm of the maximum viscosity $\eta_{\max}$ and the logarithm of the concentration c. This is expressed in the formula

$$\log \eta_{\max} = a + b \log c \qquad (1)$$

This is confirmed by HOFSTEE [1950] and PAGENSTEDT [1951].

The relation seems to be of general applicability. It holds for the data of ANKER & GEDDES [1944] with potato, corn and wheat starch, and for corn, wheat, tapioca and even for modified starches according to BECHTEL [1947]. HOFSTEE [1950] found the same relation when using the V.I.-viscograph, for unmodified as well as for modified starches. The data of MULLEN & PACSU [1942] for potato starch pasted in 30 % pyridine seem to fit the equation. The figures of different authors are not comparable of course, because different instruments were used.

From the figures of Bechtel and from the set of curves in Fig. 6, it will be seen, that at lower concentrations the decrease in maximal viscosity is much more rapid than the decrease in viscosity of the cooked paste. This means that at a definite concentration the difference might be zero and the curve is flat after reaching its maximum value. Maximum viscosity would be equal to end viscosity, whichever time of heating were chosen. From measurements with potato starch HOFSTEE [1950] was able to calculate such a critical concentration. Below this concentration there is no maximum at all. The viscosity still rises at the boiling point of the paste.

The condition of constant end viscosity is of some practical importance in industrial use. Besides using pastes of the right concentration this requirement can be met by using a dehydrating agent such as glycerol (compare Fig. 5) and by modification to a starch with a higher "critical concentration". In the section on modified starches we shall have the opportunity of discussing how this "critical concentration" can be influenced.

1.4. *The Influence of Electrolytes*

The influence of electrolytes on the pasting process is generally known. SAMEC [1912] discusses the most important points of the subject: in his handbook [1927] an extensive survey is given.

As an introduction, different examples of applications of the use of electrolytes in the starch industry will be presented. Moreover the unintentional presence of minor amounts of electrolytes is of some importance.

DE WILLIGEN [1950a] showed that concentrations as low as 0,001 N KCl and 0,0001 N $CaCl_2$ had a marked influence on the viscosity as estimated by means of the viscograph.

In the manufacture of potato starch the starch goes to the dryer with a moisture content of up to 40 or 45 %. Any electrolyte present in this amount of water accumulates in the finished starch, and has an influence on the viscosity test.

A very good illustration of this effect is also given by MEIS [1944].

Many electrolytes further the swelling of starch when present in higher concentrations. With concentrated solutions of KCNS, $CaCl_2$, $MgCl_2$ etc. the pasting can be performed at room temperature. This property is used on a commercial scale (STADLINGER [1938]). After the starch has been pasted by concentrated $CaCl_2$ the paste is extracted with dilute ethanol to remove the $CaCl_2$. The starch is dried and sold as a water-dispersable adhesive. The special merit of this procedure is that the starch grain is not desintegrated or only partly desintegrated. When it is suspended in water the paste obtained has properties resembling those of freshly cooked starch paste.

At very high concentrations of electrolytes no swelling occurs (SAMEC [1927]). For example KCNS concentrations above 4 N will not exhibit a swelling tendency on starch.

This swelling tendency of electrolytes is even more pronounced in alkaline solutions. Sodium hydroxide solutions of 0.15—1 N NaOH cause a gradual increase in swelling as shown by KATZ & DERKSEN [1930]. These preparations show typical transformations in their X-ray diagrams. At very high concentrations of NaOH again no swelling will occur (SCHOCH [1941]).

In the adhesive industry NaOH concentrations of 3 % and more are used. To a slurry in a powerful mixer NaOH solution is added and agitating is continued for some hours (O. MEYER [1942]). A sticky mass is obtained which is neutralized by the addition of nitric acid. The aim is to make a "long" glue and rigidity should be absent.

Potato starch is a favourite raw material (Köhler [1950]). Alkali processed glues of most other starches are less suited. The process involved is rather intricate and cannot be accounted for by a simple pasting. Possibly the addition of HNO_3 might have a slight oxidizing effect. A method for evaluating the "length" of such a paste is given by Erbring [1936].

From the foregoing it may be concluded that the influence of electrolytes on starch pasting is a rather intricate matter. The following influencing factors may be distinguished:

(a) The influence of low electrolyte concentrations up to 0,1 or 0,2 N.
(b) The effect of higher concentrations.
(c) The effect of very high concentrations.

These effects may be confused with that of the cation exchange (discussed in § 1. 5), with that of the hydrogen ion, and with the oxidation to which the starch is subjected at high pH.

As to the true electrolyte effects, a study has been made by van der Hoeve, Bungenberg de Jong & Kruyt [1934]. These authors estimated the temperature at which the paste had a definite but arbitrary viscosity of about 200 centipoises. The kind of added electrolytes and their concentrations were varied. As can be seen from Fig. 7, small amounts of electrolyte always lead to an increase of this tem-

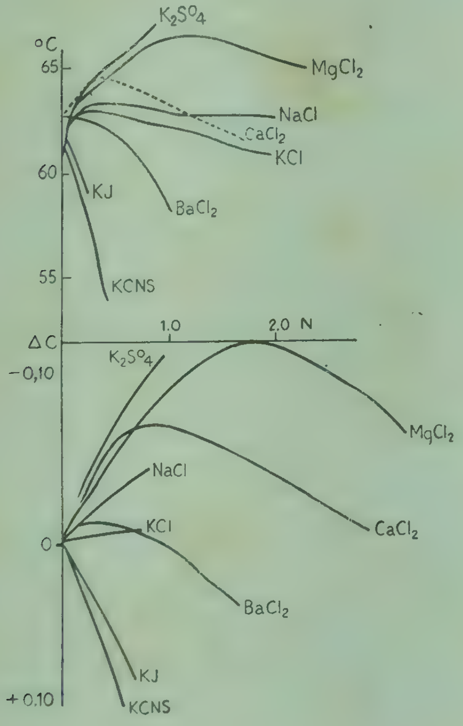

Fig. 7. [upper half] Temperature at which a potato starch paste reaches an arbitrary viscosity, plotted against electrolyte concentration. [lower half] Adsorption of electrolytes from solution at room temperature on unpasted potato starch (van der Hoeve *et al.* [1934]).

perature. The higher the valency of the cation, the stronger its effect. At higher concentrations there is a strong correlation between these variations in estimated temperature and absorption of the anions by the starch, as shown by the lower part of the figure.

It is not known if the data found by van der Hoeve *et al.* are representative for the swelling mechanism when the starch is fully pasted, and for the maximum viscosity as found in a viscogram.

TABLE 1

Data obtained with the C.I. Viscometer for potato starch pasted in solutions of K_2SO_4 and KCNS

t_1 temperature of first rise in the curve
m maximum of the curve in g/cm
η_f viscosity after cooking for 15 minutes

Concentration of electrolyte in M	t_1		m		η_f	
	K_2SO_4	KCNS	K_2SO_4	KCNS	K_2SO_4	KCNS
0.0000	64	64	1574	1574	580	580
0.0004	64	64	962	962	559	580
0.0020	64	64.5	712	679	481	519
0.0100	65	65	557	539	413	433
0.1250	66	63	529	637	423	382
0.2500	67	62	529	712	413	382
0.5000	68	58	539	847	443	372
1.0000	70	50	539	924	443	282

In Table 1 the results obtained with a Corn Industries Recording Viscometer are presented for starch pasted in solutions of KCNS and K_2SO_4 of different concentrations. The course of the temperature corresponding to an abrupt rise in viscosity is in good agreement with the value for the "temperature of fixed viscosity" as estimated by VAN DER HOEVE *et al.* In both cases the end viscosity η_f gradually decreases with increasing electrolyte concentration. The end viscosity decreases more slowly in K_2SO_4 than in KCNS, and a small increase is obtained at the highest concentrations. This is accounted for by the higher peptizing power of KCNS solutions.

Generally speaking the conclusion of van der Hoeve *et al.* that the absorption of electrolytes tends to promote the swelling and to weaken the associative forces between starch micellae is in good agreement with the hypothesis of CÆSAR [1950] that salts of the lyotropic series tend to weaken the hydrogen bonds through which the starch molecules are associated in the original granule.

1. 5. *The Influence of the Double Layer*

In the preceding subsection the ion exchange properties of starch have been mentioned. In this respect potato starch takes an extreme position. According to BRIGGS & HANIG [1946] its cation exchanging properties can be accounted for by supposing that the phosphorus is present as a phosphoric acid ester. The phosphoric acid content amounts up to 0.3 %, viz. over 4 meq/100 g, assuming that every P atom supplies one negative group only. This agrees with the ion exchange capacity found in practice.

In its native form potato starch is chiefly a potassium starch. Dependent on conditions of processing, some of these potassium ions may have been exchanged against hydrogen (lowering of pH as a consequence of microbiological processes) or calcium. The latter depends on the hardness of the water used in the manufacture.

In Fig. 8 the viscograms are given of a good quality potassium potato starch and the corresponding calcium starch. Both samples have been washed with CO_2-free water, so that the effect of any remaining electrolyte is eliminated. The difference between the curves is restricted to the maximum viscosity and the temperature, at which the maximum is reached. The point where the curve leaves the abscissae and the end viscosity are unaffected.

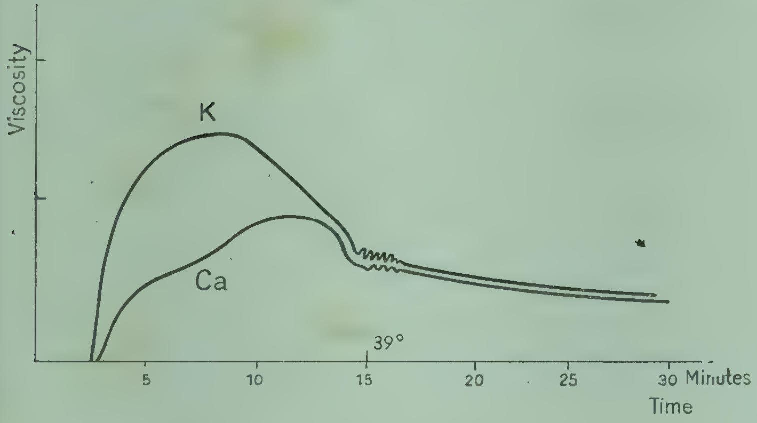

FIG. 8. Influence of exchange of $K^{\cdot}$ against $Ca^{\cdot\cdot}$ion on the viscograph curve of 8 % potato starch.

As the $Ca^{\cdot\cdot}$ and $Mg^{\cdot\cdot}$ content of the water used during processing varies from factory to factory, this is one of the causes for the variations in quality found in commercial samples.

Each industrial user will prefer his own special type. For some applications (cotton sizing, glues) the rapidly swelling K type is adapted. Other users would have difficulty in handling the high peak viscosity type of paste and therefore prefer the Ca type. In general however a high Ca content indicates inferior quality. Many users therefore prefer the K type, which can always be changed as required.

It is well known that the hydrolysis of starch is catalyzed by the hydrogen ion. When exchanging against hydrogen ions this catalyzing effect interferes with the normal pasting process. In cooking part of the starch will be hydrolysed to an extent which becomes noticeable in the viscogram. This makes the study of the explicit influence of H-ion difficult if not impossible.

A good criterion of whether any lasting harm has been done to the starch at room temperature would be the results of the following procedure:

> Starch samples are shaken with acid solutions of increasing concentration and left in these solutions for a couple of days. Afterwards the starch is washed superficially to remove most of the acid and then suspended in 1 N $KHCO_3$ solution to re-exchange the hydrogen against potassium. Finally it is thoroughly washed with carbon dioxide-free water to remove the electrolytes.

To what extent does the viscogram of these starches differ from that of the original starch? Rather high acid concentrations can be used before any difference in the rheological properties is perceptible.

Another difficulty is met when one tries to exchange the normally present potassium ion against ions of the third group of the periodic system. To obtain these elements in ionic form the pH of solutions of their salts must be rather low. Therefore these ions compete with the hydrogen ions for the occupation of the available positions in the double-layer. In the authors' experience it is doubtful if any exchange against Al occurs. At higher salt concentrations, and after thorough washing, the pH of the cooked paste gradually decreases. This points to an exchange with hydrogen instead of $Al^{\cdot\cdot\cdot}$. At higher pH or lower concentrations of salt it seems possible that some $Al(OH)_3$ is deposited on the starch. Therefore an estimation of the aluminium content of starch is not conclusive. No alterations of the shape of the viscogram similar to those of starches treated with calcium could be detected.

1. 6. *Gelification of Starch Dispersions on Cooling*

In the introduction we mentioned three aspects of starch rheology which are of major importance for industrial application. So far only the first two aspects have been discussed viz.: (1) the alterations of the rheological properties during pasting; (2) the hot paste viscosity. The third aspect viz. the change in rheological properties during and after cooling of the paste will be dealt with in this section.

The process of gelification is closely connected with what is called the "retrogradation" of starch. By "retrogradation" is meant the reorientation of more or less dispersed starch to an organised structure. From numerous publications it is known that the amylose component of starch retrogrades much more easily than the amylopectin component. SCHOCH & FRENCH [1947] nevertheless have shown that it is possible to get aggregations of the amylopectin fraction with an organised structure.

Another aspect of retrogradation is that the length of the amylose molecules plays an important rôle. LANSKY, KOOI & SCHOCH [1949] have shown that retrogradation increases when the length of the amylose decreases. The same was found by WHISTLER & JOHNSON [1948]. However with steadily decreasing chain-length retrogradation goes through a maximum and afterwards decreases.

A further factor that influences retrogradation is the degree of pasting or gelatinisation before the paste is cooled. VAN ITALLIE [1930] showed that the retrogradation as measured by X-ray diffraction and the hydrolysis by malt amylase is more intense when the pasting has been performed at lower temperatures. This might be anticipated because the more the initial orientation of starch molecules in the grain has been disturbed the more difficult will be their reorientation. The structure of the starch is not as a rule disturbed in cooking the paste. This factor obviously causes a certain microscopically perceptible inhomogeneity of the gel. This is the most characteristic property of an unmodified starch gel, as compared with gelatin or pectin jellies and also with the soluble starches.

There are so many different methods for the evaluation of starch gels that we feel obliged to restrict ourselves to the more currently used procedures.

The best defined value is the fully reversible deformation obtained under a small load (rigidity). These measurements may be performed by means of the BRIMHALL HIXON rigidometer [1939] and the BRIMHALL HIXON gelometer [1941]. The former is preferred for corn starch concentrations below 6.5 %: the latter for higher concentrations. The drawback of the former method is that it can not easily be adopted to routine measurements.

HOFSTEE & DE WILLIGEN [1950] estimated the deformation of starch gels under a load af about 13 g/cm² which they called the firmness of the gel.

The other extreme is to use a load so heavy, that the gel is ruptured. In this case, it is presupposed that the rigidity of the gel is sufficient to give a sharp breaking point (pure viscous bodies will not give a breaking point). The Brimhall Hixon apparatus can be used for determining this breaking point by using heavy loads. This apparatus especially permits the application of a steadily increasing load.

The usual instrument, however, for determining this "gel strength" is the Saare disc apparatus (EKHARD, [1929]). A disc is suspended in the paste. After cooling, the force needed to extract the disc from the gel is determined. The method has been modified and improved by HAMER [1947]. As may be seen from his article much depends on the rate of loading. It might be anticipated that the measured gel strength will be higher, the faster the rate of loading. When the rigidity of the gel is too low it may be impossible to determine a "gel strength" with this apparatus. For example, no gel strength could be determined with gels of waxy maize starch which, however, according to Brimhall and Hixon show a measurable rigidity. Measurements of gel strength of potato starch gels also are ill-defined. Probably these gels are too extensible to have a sharp breaking point.

Another type of apparatus used for measuring gel strength is the Tarr-Baker Jelly Tester. It resembles the Brimhall Hixon gelometer, but pressure is applied instead of suction. This instrument therefore belongs to a popular type of gel strength meter viz. the penetrometers.

Another gelometer of this type is the "Delaware Jelly tester".

KERR [1950] recommends the Fuchs gelometer. This instrument is of the plunger type. It consist of a hollow tube with a sharpened edge that penetrates the gel under a constant load. The time to penetrate a certain distance is measured. According to Kerr this gelometer is of good use for gels of corn starch. In the authors' experience however this instrument is less suited for potato starch gels because these gels are too extensible and too sticky.

HOFSTEE & DE WILLIGEN [1950] use a penetrometer of the plunger type (with conical plunger) and apply the load at a constant rate.

The reader will have noted that the suitability of an instrument to measure certain rheological properties of starch gels is very dependent on the type of starch.

When subjecting potato starch gel to stresses of about 13 g/cm² (the starch concentration being 8 %) and plotting strain against time, curves of the type shown in Fig. 9 are obtained. It will be seen that an instantaneous elastic deformation O A is followed by a retarded deformation from A to B. When the gel is unloaded (at time t_1) an instantaneous partial recovery BC_1 takes place, followed by a retarded recovery from C_1 to B D. The distance D E accounts for the irreversible part of the deformation. These starch gels show plasto-elastic behaviour.

The interpretation of measurements of cold paste properties by means of rotating viscometers or viscosigraphs is very complicated because the properties to be measured are so strongly influenced by the measurement itself (KERR [1950]). Measurements of cold paste viscosity by means of Stormer viscometers and viscographs (BECHTEL & KESLER [1947]) can be only of empirical value.

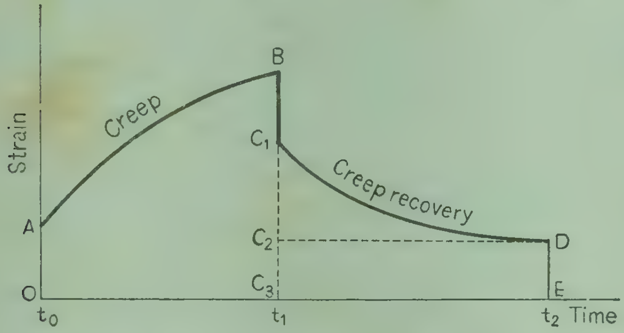

FIG. 9. Strain — time figure for a potato starch gel of 8 %.

HOFSTEE & DE WILLIGEN [1950] pasted potato starch in the V.I. viscosigraph, this pasting being interrupted at different stages in the course of the pasting. These pastes were cooled and their "firmness" was determined. The most remarkable result was that a correlation exists between the shape of the viscosigram and the "firmness" of the gels obtained. The same holds for the gel strength as measured by means of a conical penetrometer.

BRIMHALL & HIXON [1939] also state that, as a rule, rigidity and gel strength parallel each other.

Addition of sugar enhanced gel strength up to an optimum of 50 g saccharose per 100 g of an 8 % starch paste. (WHITTENBERGER & NUTTING [1948]). Microphotographs of pasted starches and normal photographs of gels made from these pastes suggest that firm gels are obtained when the swollen grain is intact and is not swollen to a high degree.

In I, 1, 2 pasting in glycerol solutions is discussed. Gels obtained from these cooled pastes showed an increase in firmness (rigidity) and gel strength up to 50 % glycerol (Fig. 10).

Another factor that influences the rigidity of gels has been discussed by BRIMHALL & HIXON [1939]. The rigidity was found to rise sharply at one distinct concentration when the latter was increased (Fig. 11). This concentration was lower the higher the pasting temperature. Bearing in mind that the lower the pasting temperature the less the swelling will be, it may be anticipated that more starch is necessary to give a coherent gel after cooling when the pasting temperature is low.

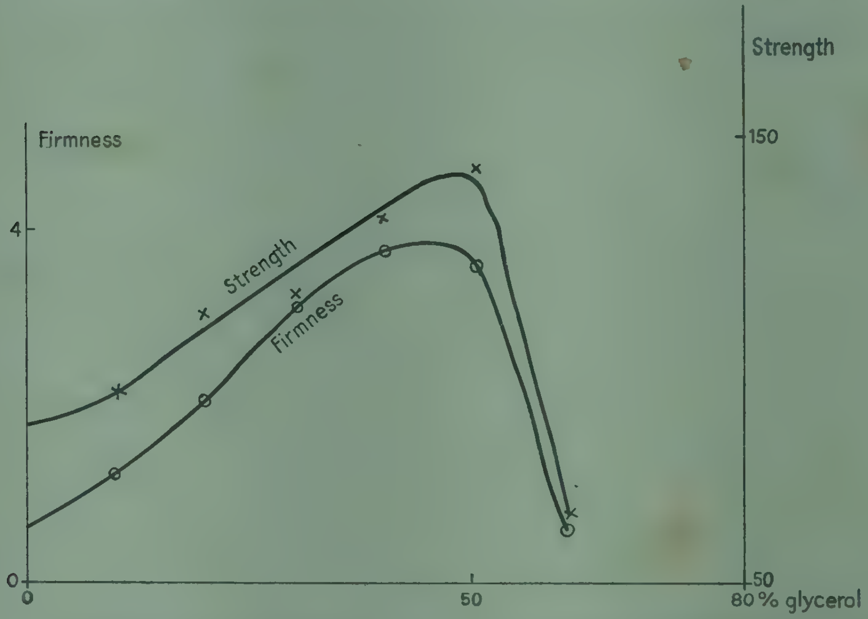

FIG. 10. Firmness and strength of potato starch gels made with different glycerol concentrations.

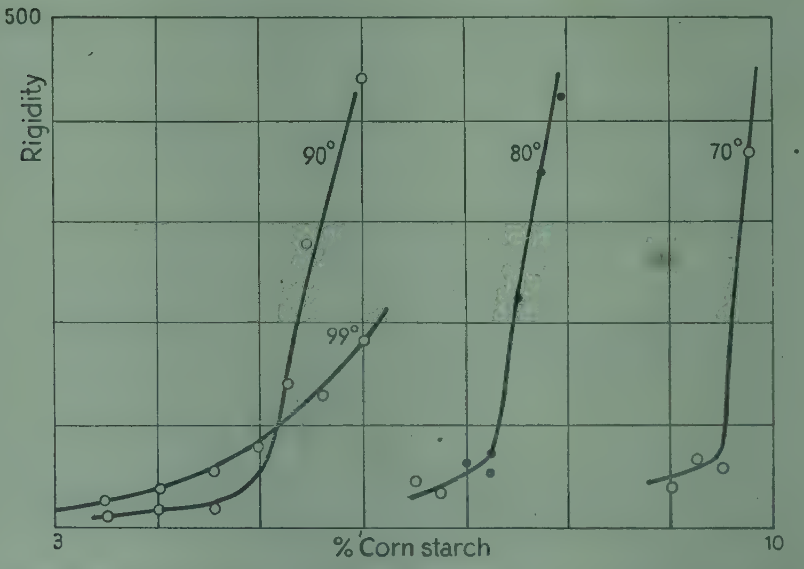

FIG. 11. Rigidity of corn starch gels of different concentration (BRIMHALL & HIXON [1939]).

The critical concentration therefore would be that concentration at which the volume ratio of swollen starch to dispersing liquid is such that the particles of the initial suspension are immobilized and the whole behaves like a gel. Gels obtained from pastes made at higher temperatures than about 90° C show less sharp increases in rigidity. Gels from pastes made at 120° C show hardly any rigidity because their degree of dispersion is too high to set to a gel as in the case when the paste was subjected to high shear.

WHITTENBERGER & NUTTING [1948] found an almost linear dependence of gel strength on concentration (concentration between 6 and 11 %, pasting temperature 90° C). Brimhall and Hixon's results show a linear relationship between starch rigidity and concentration within the limits of 5—6 % at a pasting temperature of 90°.

In the authors' opinion there is a striking correlation between factors that influence retrogradation and rheological properties of starch gels (firmness, rigidity and strength). The following picture might account for the different facts.

A certain degree of swelling is necessary to get a coherent gel. When the degree of swelling is too low, a suspension of more or less swollen starch grains will result and the available water is not fully immobilized. In more advanced states of swelling a coherent and firm gel may be obtained, but part of the water is squeezed out on cooling (syneresis). There is a certain degree of swelling that is optimal for the formation of firm and strong gels. Afterwards, as a consequence of a higher state of dispersion, the firmness and strength of the gels decreases (HOFSTEE & DE WILLIGEN [1950]). Cooked pastes of potato starch have as a rule passed the optimal state of swelling. To make pastes more suitable to give strong gels the swelling must be hindered, e.g. by adding dehydrating agents such as saccharose or glycerol. Other means of getting a retarded swelling will be dealt with in I, 3 and 4.

From what has been said so far one would conclude that highly dispersed starch, whatever its mode of preparation, would not give solid gels. This is confirmed by an experiment of WHITTENBERGER & NUTTING [1948]. An 8 % starch suspension was pasted and subjected to high mechanical shear at 75°. None of the samples did set to a gel, even when sucrose was added. It was concluded that the persistence of undisturbed swollen grains was essential for gel formation.

The statement of WHITTENBERGER & NUTTING [1948] that electro-

TABLE 2

Comparison of the properties of pure $Ca^{\cdot\cdot}$ starches with those of pure $K^{\cdot}$ starches made from the same commercial starch samples of 1950 harvest. Values are averages of 69 samples. Methods used according to HOFSTEE [1950] and HOFSTEE & DE WILLIGEN [1950]

	$Ca^{\cdot\cdot}$ starches	$K^{\cdot}$ starches
Maximum of the viscosigraph curve	48	88
Viscosity after 10 min cooking	21	23
Jelly strength after 24 h at 0°	88	91
Rigidity under same conditions	121	78

lytes diminish rigidity and strength of the jellies may be confirmed.

A strong influence of the cation content of the starch can be found in some circumstances. An example is given in Table 2. This refers to 8 % potato starch cooked for 15 minutes. The Ca starches give a much more rigid structure in this case. Probably the divalent ions strengthen the structure of the swollen grains, so that the remains of this structure have a more important influence than in the corresponding K starch jellies. But this will depend on the treatment of the hot paste and on the origin of the starch.

The influence of pH of the paste on gel properties will be discussed more extensively in a later section. In the meantime it is interesting to note that retrogradation as well as gel strength are promoted by a moderate lowering of the pH.

At the end of this subsection the authors wish to stress the point that gel rigidity and gel strength do not always go parallel. The differences in the course of their magnitudes may afford a good means for the disclosure of properties not distinguishable by measurements on the warm paste.

2. Different Types of Starch

2. 1. *Difference between Grain Starches and Root and Tuber Starches*

In general the various kinds of more common starches show gradual differences only (KATZ *et al.* [1938]). Potato starch however takes a rather extreme position, as will be shown in the following examples.

In Fig. 12 the viscosigrams of 7 kinds of starch are given as recorded by the V.I. viscosigraph (DE WILLIGEN *et al.* [1948]). Potato starch shows a much higher peak. But this is not a characteristic property of potato starch exclusively. The same type of curve can be obtained with corn starch at higher paste concentration (Fig. 13).

The difference is that the high peak viscosity of potato starch is obtained at a much lower concentration, which is in a range used commercially.

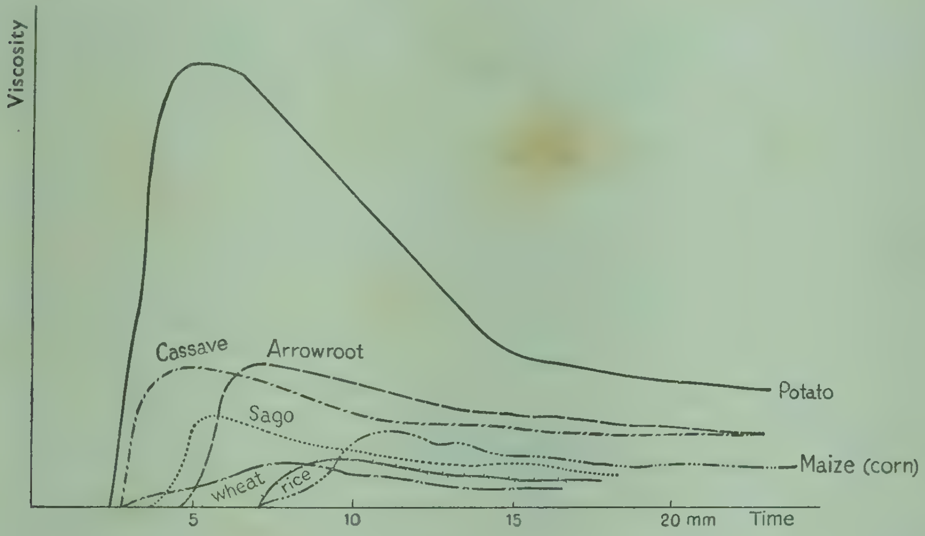

FIG. 12. Viscograms of different kinds of starch (DE WILLIGEN *et al.* [1948]).

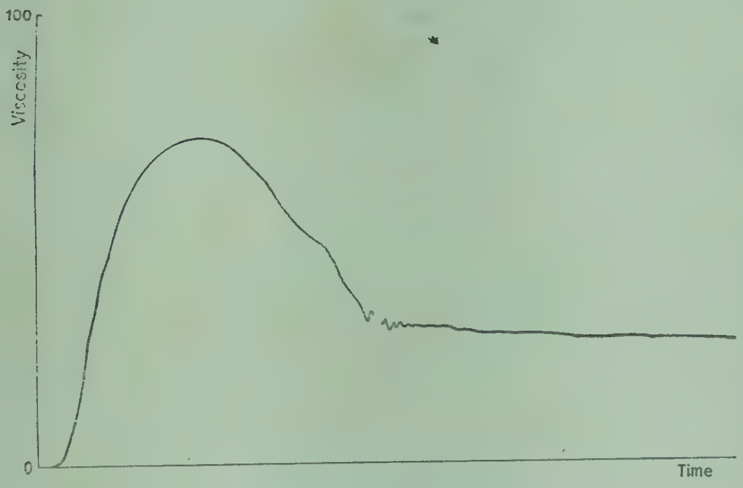

FIG. 13. V. I. viscogram of 16 % corn starch.

Although many scientists (SAMEC [1927], KATZ [1938], BEAR & FRENCH [1941]) have tried to give an interpretation of the differences between various kinds of starch, no clear cut picture has been obtained. No effort will be made here to discuss the subject in detail. Rather a concise summary of different points related with the rheological differences will be presented.

As to the differences in composition, two groups of minor constituents might be of influence. SAMEC [1927] has accentuated the importance of the P-content. Later it has become obvious that P can be present in two different forms, viz. (1) as an ester of starch and (2) more loosely bound as a phospholipid. Beside these phospholipids some starches may contain other fatty material (SCHOCH [1942], MIKUS, HIXON & RUNDLE [1946]; and others).

SCHOCH [1942] has extracted different starches with 85 % methanol and got the results shown in Table 3. The extreme position of potato starch is clearly shown. It contains no fatty acid and has the highest P-content. This P is not extracted. It has been shown that P is present as a mono-ester of starch (BRIGGS & HANIG [1946]).

TABLE 3

Analysis of starches before and after extraction with 85 % methanol (SCHOCH [1942])

		Potato	Corn	Wheat	Rice
Fatty acids	before	nil	0.84	0.50	0.59
	after	nil	0.12	0.03	0.03
Nitrogen	before	—	0.34	—	—
	after	—	0.21	—	—
Phosphorus	before	0.095	0.12	0.03	0.03
	after	0.084	0.015	0.008	—

Table 4 presents a survey of the differences in physical properties of starches. Again the extreme position of potato starch is striking. The classification of KATZ [1934b] in accordance with the X ray diagram is closely correlated with the ability of the starch to absorb and deliver moisture. In a qualitative sense the same holds for the sedimentation volume. The swelling—as measured by the sedimentation volume—correlates positively with the heat of gelatinization. For the attainment of a higher state of swelling—a lower state of association—a larger amount of heat is necessary. That the initial structure of the different starches is the better preserved the less its heat of gelatinization, is clearly shown by mere microscopic observation. In potato starch after pasting at 100° only a few fragments

TABLE 4

Comparison of physical properties of different starch varieties

	Potato	Sago	Tapioca	Arrow-root	Corn	Wheat	Rice
Type of X-ray diagram . .	B	C	C	C	A	A	A
Sedimentation volume at 75°	very high	—	—	154	80	80	—
Moisture uptake mg/g at at relative humidity 86 % and 23° C	290.3	240.9	—	240.0	226.2	228.4	—
Moisture loss if relative humidity is lower by 10 %	27–30	22–23	—	22–23	20–21	20–21	—
Heat of gelatinization in cal/glucose unit	9080	—	8780	—	7300	7100	5700
Gelatinization temperature °C	61.5	—	63.5	—	65.0	68.5	75.0
Mean size of starch grain in μ	35	—	16	—	16	13	4

of grain structure are found. Rice starch paste, on the contrary, contains a fair amount of grains in a much less swollen state.

The rheological properties are for the most part dependent on the degree and the rate of swelling. Many industrial applications are based on this point. Cereal starches are preferred where a short paste is wanted, rice starch especially is difficult to disperse (an advantage in collar starching). Corn starch is especially adapted for household pudding making.

Mullen [1942] suggests that the differences might be explained by the size of the grain. This however is not very probable. For example tapioca and corn (maize) would be expected to have almost identical properties. This certainly is not true. Samples of potato starch of different grain size also showed no large difference in viscosigraph curves (de Willigen [1948]).

2. 2. *Starches with Extreme Amylose-Amylopectin Ratios*

In the introduction it has been remarked that starch consists of two main components viz. the amylose, with straight chains, and amylopectin, with branched chains. Amylose associates (retrogrades) readily, but amylopectin only under much more rigidly defined conditions (low temperatures, addition of methanol) as shown by Schoch

& French [1947]. Amylose solutions are unstable and set to gels at higher concentrations, but amylopectin solutions are stable and 8 % solutions do not show any consistency when studied in the V.I. viscosigraph.

As a result of biological research, two extreme types of starch have been obtained. The one has a very high amylopectin content (almost 100 %) and is represented by the different kinds of "waxy" starch. (Hixon & Sprague [1939]). The other type has a high amylose content. So far this class contains only the wrinkled peas (Hilbert & MacMasters [1946]) and the sugar corn (Dvonch *et al.* [1951]). In Fig. 14 the viscosigram of an 8 % waxy maize starch suspension and an 8 % wrinkled pea starch suspension are shown. It will be noted that the viscosigram of wrinkled pea starch is perfectly flat. The shape of the viscosigram can be derived principally from the state of swelling of the starch grain (I 1. 2). Therefore it seems reasonable to suppose that the wrinkled pea starch swells with great difficulty. This is confirmed by the following observations. Starch suspensions (8 %) heated for one hour at 95° C have the characteristics of a suspension rather than of a paste. Even after heating for 1 hour at 120° C some of the grains still display birefringence. A gel obtained after heating the starch suspension at 95° C shows a strong syneresis. At the same time the "waxy" corn starch has a distinct viscosigram in contrast to amylopectin obtained from dispersed potato starch. Waxy corn has an organised structure as revealed by its X-ray diagram (Kerr [1950, p. 159]). Amylopectin obtained by fractionation methods may be considered to be amorphous (Kerr [1950, p. 187]).

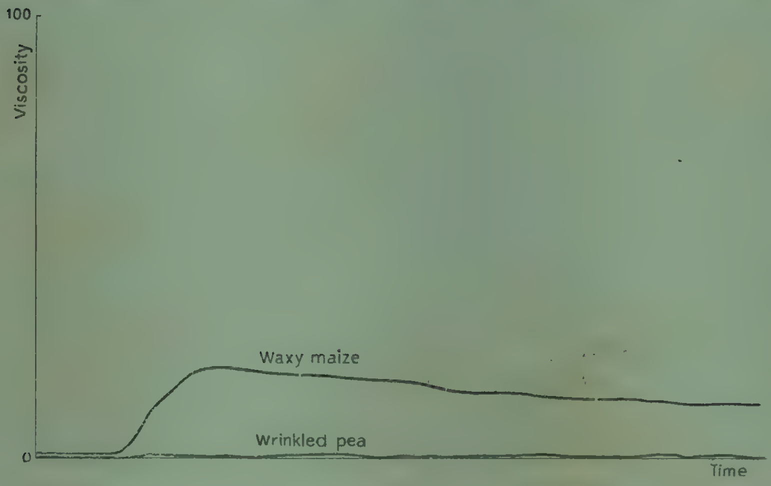

Fig. 14. Viscograms of waxy maize starch and wrinkled pea starch (8 % suspension).

> As shown by BRIMHALL & HIXON [1939] waxy maize starch pastes have a low rigidity after cooling. Glues made of waxy starch therefore do not "set back". This makes waxy starch especially suited for the manufacture of certain types of glue. When applied by spreader rolls or brushes this glue does not "roll".

The swelling phenomenon therefore seems to be connected with this organised structure. This is confirmed by the experiments of SCHOCH & FRENCH [1947], who obtained preparations from amylopectin made by fractionation, comparable with native waxy starch. It was shown that these particles showed the phenomenon of swelling when heated in suspension.

Comparing "waxy" starch with wrinkled pea starch it is clear that the structure of the former is more easily disorganised than the structure of starch with a high amylose content, because the swelling leads to a complete dispersion or the elimination of the associative forces. It seems reasonable to suppose that straight chains will associate more easily than branched chains. This supposition is confirmed, moreover, when the behaviour of amylose solutions is compared with that of amylopectin solutions.

The more common starches may be supposed to occupy an intermediate position with respect to their rheological properties as a consequence of their intermediate composition. This is indeed the case (BRIMHALL & HIXON [1939]). The mutual differences of this class of starches cannot be explained by their differences in composition but may be interpreted as a difference in their degree of associations as suggested by SAIR & FETZER [1944] or to a minor degree by their content of non-carbohydrate compounds.

3. Degradation of Potato Starch during Processing, in Storage and at Higher Temperatures

As a rule any degradation of starch is irreversible. The only possibility of getting an undegraded product is to avoid circumstances which promote the reaction. This holds especially for the processing of potato starch. Numerous qualities are offered commercially, differing in rheological properties, because of unfavorable factory conditions.

The aim of starch manufacture is a separation of the starch from the accompanying biological material, viz. cell wall and soluble cell content. The walls are ruptured by rasping. Sieving out the fibrous material is the next stage, after which the starch is separated from the fluid by centrifugal separation methods or by gravity settling, this last method being more and more replaced by the former.

In potato starch factories circumstances are generally favourable for a development of micro-organisms. Their action may be diminished by fast processing. In the older German process ("laveure"), with its 24 hours' settling period, more alterations occur than on the "Dutch tables", where starch does not normally stay for more than 4 hours. In the centrifugal process the starch can be separated from the fluid within some 10 minutes. In warm weather the starch is much more liable to bacterial influence than in winter time. Especially bad conditions are met when the production is interrupted during warm September weather.

> In factories using gravity settling methods a certain amount of starch is left over in the wet state from Saturday evening until Monday morning. Table 5 compares the properties of starches made from this residue with the normal product of the same factory. There is a possibility that enzymes from the potato juice also influence the starch.

TABLE 5

Comparison of samples taken on Monday with those taken on Thursday in a factory using the "Dutch tabling process" (DE WILLIGEN, *et al.* [1948]). Mean values for all samples taken at weekly intervals from 8/9 until and including 3/11 1947. Viscosity values in degrees, taken from V. I. viscograph (maximum of the apparatus 350°). The pH is measured in the water from which the sample was worked up

Sampling place and day		Maximum viscosity	pH
No 1	Monday	291	6,12
	Thursday	325	6,02
No 2	Monday	230	4,77
	Thursday	258	5,24

Under normal conditions starch suspensions show dilatancy. Higher concentrations are free-flowing but stiffen as soon as pressure is applied. This is an important property in the "tabling" process, because then it is possible to scoop the settled starch with a shovel. After some seconds the cake flows freely off the blade. This property is dependent on the grain diameter and the water content. But the more important factor is the amount of degradation during processing. Contamination with protein has the same effect.

Another practical property, possibly related to dilatancy, is the particular "crunch" of the dry starch. The powder has a firm touch on sqeezing with the fingers in not too thin a layer and it has a certain compactness, which prevents it from flowing freely. This property is very much dependent on small changes in humidity (probably the most important factor in establishing the necessary conditions for "crunch"). But a degradation during the manufacture sometimes diminishes this property to a rather remarkable extent.

Products which have been stored for some time in the wet state ("thirds") never have the right crunch. But this can be caused by contaminations (proteins, calcium phosphate etc.). If a free-flowing starch is wanted a small amount of a substance like calcium phosphate is added.

At ordinary storage temperature, potato starch is not at all stable. Within some months, part of the P-content is given off in inorganic form (DE WILLIGEN [1947]). At the same time the viscosigraph curve is changed. The starch swells less rapidly than before, and consequently the slope of the first part of the curve is diminished. In most samples the maximum of the curve is lowered and shifted to the right.

The cause of this change is not at present known. It is probably not a result of bacterial or enzymatic action and no influence of impurities has been found (DE WILLIGEN [1950b]).

Users of potato starch are warned not to depend on a constant quality during storage. For several procedures, e.g. alkali glue making, the formula will have to be changed in the course of every production season, as soon as starch from newly harvested potatoes comes in.

It is well known that the swelling properties of potato starch are greatly altered by heating it in a moist condition under such circumstances that no gelatinization occurs (WIEGEL [1933]; GALLAY [1936]; SAIR & FETZER [1944]; WHITTENBERGER & NUTTING [1948]). GALLAY suggests that even during the processing of corn starch there might be a change in this direction (the authors however have not been able to confirm this). The maximum of the viscosigram is lowered and shifted to the right, the viscosity of the cooked paste is raised. In fact, this is a case of change of the critical concentration mentioned in I, 1.3. This value can be raised to 8 or 9 %. The viscosigram resembles that of a cereal starch. Moreover the gels from these starches are quite similar to those of cereal starches (Whittenberger & Nutting [1948]). Sair & Fetzer [1944] state that besides having an X-ray diagram of the A type, these heated starches show a marked decrease in sorptive capacity.

This is in favour of the opinion, stated in I, 2. 1, that the rheological differences between the species of starch are not fundamental. The instability of potato starch then would be a consequence of its labile structure in comparison with cereal starches, e.g. rice starch (Sair & Fetzer [1944]).

In Fig. 15 some examples are given of viscosigraph curves of heated starches. Fig. 16 is a microphotograph of such a starch heated in the Corn Industries Recording Viscometer for one hour (in 8 % concentration, the stirrer turning at maximal velocity). The grains have been deformed, but in comparison with the final stage of Fig. 4 only a small number has been broken.

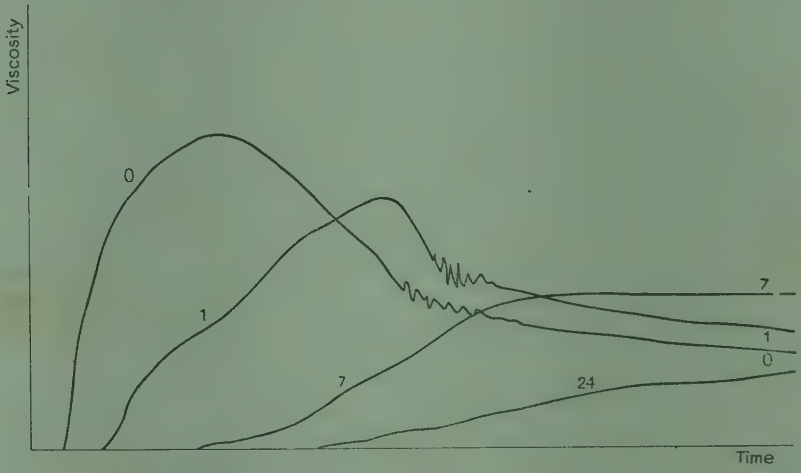

Fig. 15. Viscograms of heat-moisture treated starches. The numbers give the heating time in hours.

4. Starches Modified by Wet Methods

Besides being used as such, starch is modified in several ways to suit the many specific purposes of the consumer. It would lead us too far away from the main subject to discuss the rheology of all these products. We prefer to restrict ourselves to the most important methods, and so a more general rather than a detailed picture will be presented.

In the U.S.A. a fair amount of the corn starch is subjected to an acid treatment, and no clear distinction is made between natural starch and these modifications. The only way in which the starches are characterized is by their "fluidity".

Pre-gelatinized starch, which swells in cold water, is used for a number of applications, e.g. as an addition to paper pulp in paper manufacture. It is made by bringing a starch slurry on onto a drum dryer so as to gelatinize and to dry the paste in one cycle. The starch manufacturer has to realize the exact degree of gelatinization suiting the requirements of a particular paper manufacture: the starch grain must be sufficiently swollen to give a good sizing. On the other hand the dispersion has to be limited to such a degree that the starch is not drained off during dehydration on the "wire". It may be assumed that the rheological properties of these starches compare with those of the original starch. Any amount of wet modification may precede gelatinization. (For cold pasted starches see I, 1. 4.)

Acid-modified starches. As long as the crystal structure of the starch grain is intact, hydrolysis takes place by the preferential attack of the amorphous spots. This is clearly demonstrated in the case of amylodextrin.

> Amylodextrin is a starch that has remained for months in 15 % sulphuric acid. The mean degree of polymerization has gone down to 25 (from at least 200 for amylose and several thousands for amylopectin). Notwithstanding the sharpness of its X-ray diagram and its optical anisotropy are not affected. This may be accepted as a proof that the crystalline parts of the granule have not been attacked (KERR, [1950, p. 158]).

Another evidence for the preferential attack of the amorphous spots is found in the way in which the pasting of the starch proceeds. As soon as the swelling begins a lack of coherence is evident. Simultaneously with swelling, the grain falls into pieces, and so a state of good dispersion is reached at a much earlier stage than with the unmodified product. The reader will not be surprised that the maximum viscosity is decreased by an acid treatment and likewise the viscosity of the cooked paste. As a matter of fact a degree of modification can be realized where the warm solution is a clear, only slightly viscous, liquid.

If the starch molecules are hydrolized to a limited extend only, the retrogradation of the paste increases (LANSKY *et al.* [1949], WHISTLER & JOHNSON [1948]). The thin hot pastes gelify to firm and rigid gels.

Depending on the treatment a gel strength can be obtained, which is much higher than that of the unmodified starch gel.

The structure of these jellies seems to be quite different from that of the unmodified starch. In the latter case an important part of the structure is formed by the remains of the granules. The inhomogeneity is clearly visible under the microscope. In the acid modified starch jelly the grains are divided into much smaller parts and gel structure must be formed from much smaller units.

A very instructive experiment in comparing starches of different modification is given by KESLER & BECHTEL [1947]. The starches were cooked in the Corn Industries Recording Viscometer and cooled in the same instrument, the stirrer proceeding throughout at the same rate. An unmodified corn starch in 5 % concentration reached a hot paste viscosity corresponding with 150 g-cm torque and a cold paste viscosity which was only slightly higher. Probably the stirrer disturbed whatever structure was present or formed during cooling. All acid modified starches in concentrations of 7—23 %, had warm paste viscosities below 100 g-cm. But notwithstanding the heavy stirring the cold paste viscosity reached 5—10 fold values within the first hour.

The low hot paste viscosity would make the starch suitable for all those purposes where a high dry matter content of the starch is wanted, as in paper coating. However its liability to retrogradation restricts its use in coating machines.

Oxidized starches. The aim of starch oxidation is often the same as that of acid treatment, viz. the preparation of starch with a low hot paste viscosity and a fairly good cold paste body. Practical arguments then determine the choice of the treatment. Potato starch pastes have an objectionable taste and odour, which is intensified by acid treatment. The fatty acid containing starches (e.g. corn starch) may develop rancidity which is removed by oxidation. The colour is improved. An oxidized starch in this respect gives a more desirable product for incorporation in food products.

For the industrial preparation of such starches, a number of oxidants can be used, the most important ones being hypochlorite, hydrogen peroxide and chlorine. The modified product is said to have a lower hot paste viscosity, increased adhesiveness and a lower rate of congealing (Newton & Peckham, in KERR [1950]).

A thorough investigation of the oxidation of corn starch with hypochlorite has been published by FARLEY & HIXON [1942]. It is assumed that the attack is restricted — at least in the first stage — to the amorphous spots, just as in the case of acid treatment. At first there is an increase in the hot paste viscosity and in the swelling powder. Both values decrease after an optimal stage of the treatment. The rigidity decreases at the onset, however short the treatment. A patent by KERR [1935] claims the production of starches with maximal hot paste body and low cold paste body. These facts do not fit in our general concept of starch oxidation.

As a matter of fact it would be wrong to generalize these results to treatment of other starches e.g. potato starch, or with other oxidizing agents. Our experience is that the oxidation of potato starch always leads to an increase in gel rigidity. Indeed this is the normal procedure for making pudding powders from potato starch.

Treatment with aldehydes. The reader is now supposed to be familiar with the high peak viscosity of potato starch, and with the interpretation of the decrease as a gradual breaking down of the starch grain. For certain purposes it is favorable if the rate of swelling can be maintained and the rupture of the grain prevented. This may be realized by means of a treatment with aldehydes (ROWLAND & BAUER [1938]; KERR & SCHINK [1948]; MÖLLER [1943]). A viscogram of such a modified starch is given in Fig. 17. It is assumed that resistant

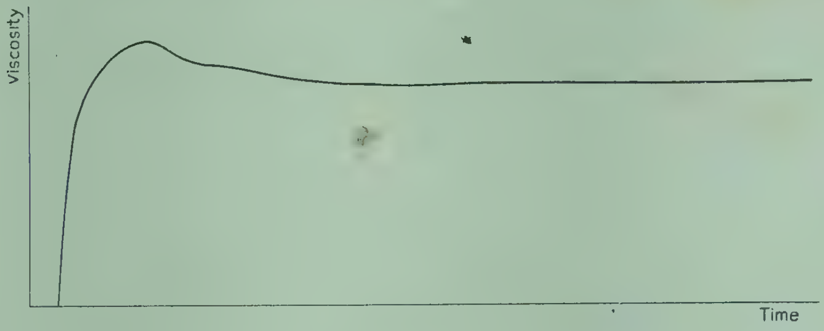

FIG. 17. Viscogram of an aldehyde starch.

bonds are formed between starch molecules by means of methylene oxide bridges. The organization of the granule structure is strengthened in this way so that it can withstand the disrupting forces. However a too rigorous treatment may interfere with the swelling. We presume that in this case water uptake is hampered as in the case of glycerol addition.

Starch ethers. The most recent method of modification is the coupling of starch with ethylene oxide, ethylene chlorohydrin, monochloroacetic acid, acryl cyanide etc. (CHOWDURRY [1942], KESLER & HJERMSTADT [1950], LOLKEMA [1949], MÖLLER [1950]). This leads to an increased branching of the starch molecules and, as a consequence, the retrogradation is prevented or much delayed. It is possible to get modifications of potato starch with the same viscogram as that of the original starch, but without retrogradation on cooling. The cold pastes are almost as clear as the warm paste, hardly showing any increase in viscosity with time.

CHAPTER II

CEREALS

BY

D. H. GREUP AND H. M. R. HINTZER
CEREALS DEPARTMENT OF THE CENTRAL INSTITUTE FOR NUTRITION RESEARCH T.N.O., WAGENINGEN, NETHERLANDS

0. Introduction

In cereal technology a great variety of rheological problems is found. Starting with the milling process, the brittleness of the branny cover of the kernel and the pliability of the germ are of major importance. Viscosity, elastic modulus and tensile strength are the outstanding factors in determining the behaviour of wheat flour dough, whereas compressibility, crispness and breaking strength of the baked products play their role in acceptability to the consumer.

Since chiefly wheat flour doughs have so far been investigated and the main part of wheat flour is utilised in the manufacture of bread, it is proposed to deal in this chapter with the various rheological aspects of wheat bread making. A short description of the mixing, fermentation and baking process and of the properties of bread will be given first (II, 1), followed by a discussion of the fundamental nature of dough (II, 2). In the remaining parts the relation between rheological properties and the behaviour of dough during mixing, fermentation and baking, and the characteristics of bread crumb will be described (II, 3) as well as the commercial evaluation of baking value by means of measurement of dough properties (II, 4).

1. Bread Making and the Rheological Phenomena Involved

The numerous reactions and processes involved in bread making may be mainly divided into three groups, namely mixing, fermentation and baking.

The objective of the *mixing* process is to hydrate the gluten and the starch and to incorporate uniformly the various dough ingredients. By the action of the mixer arms the dough film, formed at the interface or boundary line between the water and the flour, is broken up and new flour surfaces are exposed to the water. When all the flour particles have been wetted, the water exists in all degrees of absorption from that of the nature of bound water to that, which has the characteristics of a film in which the molecules have freedom of motion.

A proper mixing of the dough also involves a so-called development, which may mean principally the formation of a complete gluten network of thin strands. The protein particles absorb water and, by drawing together, form very fine strands, which permeate the dough mass. In the kneading process the gluten strands are stretched and rearranged into a parallel pattern. At the same time the gluten fibrils are criss-crossed and wound about the starch granules producing a 3-dimensional continuous mesh network, in which the starch granules are enclosed. During this process there is an apparent imbibition of water, as evidenced by a decreasing dough mobility. If mixing is continued beyond the stage of minimum dough mobility, the dough is "broken down" from a firm dry coherent elastic mass to one having properties of slackness and lack of tensile strength.

After mixing the dough to optimum development, *fermentation* is started in order to aerate the dough and to produce a porous structure. During this period the necessary cell structure has to be built up. The dough is usually allowed to ferment to a large volume, then worked down and allowed to rise again, a process which is repeated one or more times.

Two groups of forces are operating during the fermentation process: those of gas production and those of gas retention. These forces work simultaneously and interact with one another. Gas producing capacity depends mainly on the availability of fermentable sugar, whereas the gas is generated largely by the action of several enzymes of which amylase, maltase and zymase are the most important. Gas retaining capacity is determined by the quantity and physical condition of the gluten. The ideal adjustment of all forces influencing gas production and retention would cause the maximum production of gas to be reached in the same length of time from the start of fermentation as the optimum gas retention.

Usually there is a range of fermentation time over which the two groups of forces are in balance with each other. This range is called "the fermentation tolerance". The rheological properties of the dough and the change in these properties during fermentation, which will be dealt with more extensively in II, 3 are of marked influence on fermentation tolerance.

After fermentation the action of heat during *baking* produces many alterations in the physical properties of the dough. As the temperature is elevated an increase in volume of the gases is caused by thermal expansion, by the increased rate of fermentation and the evaporation of water and other volatile products and by the gas becoming less soluble. This results in an elastic and plastic expansion of the dough, known as "oven spring". Meanwhile, a softening of the gluten and a plasticization of the starch takes place until this softening process is arrested by the swelling of starch at a temperature of about 58° C. The starch granules increase in volume and become more and more fixed in location, moving only with difficulty as further stretching goes on. Water is taken from the gluten by the starch as a result of which the gluten strands are strengthened. Their viscosity is raised and their tensile strength increases. The starch swelling is largely completed within a very short period of temperature rise.

A steady increase in pressure occurs in the dough until the point is reached where the tensile strength of the dough bubbles is exceeded. The bubbles puncture or break and the rate of oven spring decreases. The expansion of the dough finally ceases during the gluten coagulation, starting at a temperature of about 75° C. Finally, the partly gelatinized starch and the coagulated gluten permanently fix the structure.

During the initial period of baking, the rise of temperature has an accelerating effect upon the action of the enzymes. Further rise in temperature slows and finally inactivates the enzymes. On the outer side of the dough mass, by the action of heat and steam on starch, dextrins are formed, which are mainly responsible for the glaze and bloom on the crust.

Among the chief characteristics of *fresh bread* are the compressibility and elasticity of the crumb (softness, tenderness), and the brittleness of the crust. These desirable properties are rather rapidly lost during storage and form part of the many alterations taking place when bread ages. The whole complex of phenomena is usually referred to as "the staling of bread". The decrease in compressibility as bread ages provides a mechanical basis for following the process of staling. Hence many devices have been employed for measuring the changes in the force-deformation relationships of the crumb. The most widely used method is the measuring of the crumb "softness" (deformation under constant load). More recently however attention has been drawn to the measurement of crumb "firmness" (load required to produce constant deformation). The results of the two methods, which will be dealt with later, cannot be compared by the simple use of reciprocals.

2. Rheological Fundamentals and Flour Dough

A dough resembles a solid in that it has elastic properties (dough tends to spring back when the deforming force is removed) and a liquid in that it will flow (a dough ball will gradually flatten out).

When a dough is deformed by force, the stretch is partly elastic and partly plastic. Hence on removing the deforming force, recovery is not complete. The elastic deformation will disappear but there will remain a non-recoverable deformation due to viscous flow. Investigations into the nature of the physical properties of dough have revealed that the elastic properties are due to the spring-like structure of the protein chains. The linkages between these protein chains are not equally strong at all points, however. On extending, some of them break, causing plastic deformation, while others which are responsible for the elastic recovery remain intact. These alterations have to take place in the presence of a starch-water mixture. As this mixture, although primarily fluid in character, also possesses some rigid properties, a complete relaxation of even those protein chains which are capable of truly elastic recovery, is made impossible. Flour dough thus appears to be an exceedingly complex system and since baking quality is largely determined by a number of separate physical properties, many methods have been developed to evaluate baking quality by physical measurements. These measurements were made on the more simple flour-water suspensions, on crude wet gluten washed from the flour and on flour doughs. The majority of the instruments devised, however, either measured one of the properties only, or a complex reaction of many factors acting together. In both cases the results are often misleading.

Although a number of the instruments proved their value in assessing baking quality (for description, see II, 4), the more theoretical background of the problems remained unrevealed. In this section, attention will mainly be given to the investigations of a more fundamental nature, in which definite physical constants are separated and individually measured. For a complete survey of the extended literature on the subject of dough properties the reader is referred to the excellent reviews of BAILEY [1940] and SWANSON [1946].

One of the first dough testing machines, measuring specific physical dough properties, is described by KOSUTÁNY [1907, p. 249]. A piece of dough was extended at a constant rate and the stress required to produce the extension was registered. Strangely enough, no further attempts in this direction were made during the following twenty-five years.

A major contribution to the knowledge of the fundamental nature of dough was made by SCHOFIELD & SCOTT BLAIR [1932b, 1933a, b, 1937a], who investigated the elastic and plastic properties of flour dough and the relationship existing between them. By the use of a special dough stretching apparatus they were able to measure certain specific physical properties in absolute units.

Their first experiments were carried out with an instrument for measuring plastic strength under rolling, the so-called pachimeter (SCHOFIELD & SCOTT BLAIR [1932a]). Stress, however, could only be applied for a fraction of a second, whereas in baking the stresses set up by the gas operate over several hours.

A second instrument, the "rack", was accordingly designed, which permitted applying a stress over longer periods. In this instrument a cylinder of dough, extruded from a metal gun, is stretched out and held stretched for a measured time at the end of which the dough cylinder is cut loose and the elastic contraction measured. Elastic recovery was found to increase with the percentage of extension up to 100 % and to be a function of the time under stress. Since the time during which stress is applied and the magnitude of the stress are both significant in determining the amount of elastic recovery, a formulation based on Maxwell's relaxation time was thought to be of value in this connection. In a partly viscous material, stress will dissipate gradually with time and Maxwell assumed a proportionality of this rate of dissipation to the stress. The reciprocal of the proportionality factor is called by Maxwell the time of relaxation: (t_r). Relaxation time can easily be shown to be equal to the ratio of viscosity to shear modulus.

It should be remembered that in practice the viscosity of a dough never stays constant during an extension, so that the viscosity must be regarded as a mean viscosity. For dough the shear modulus, given by the ratio of shearing stress to shearing strain, is equal to one-third of Young's modulus, since Poissons's ratio is approximately $^1/_2$. For convenience this shear modulus will be referred to as the "modulus" throughout this chapter.

In the case of dough, relaxation time is not a constant independent of stress. Experiments with "the rack" showed that t_r decreases as an exponential function of stress. Consequently an extended significance was given by Schofield and Scott Blair to Maxwell's time of relaxation so that the expression for the relaxation time, as given by the ratio of viscosity to modulus, could be applied to dough.

Most of the work however was done with the extensimeter, which can be used in several modifications (SCHOFIELD & SCOTT BLAIR [1934]). Fig. 1 illustrates the principles of this instrument.

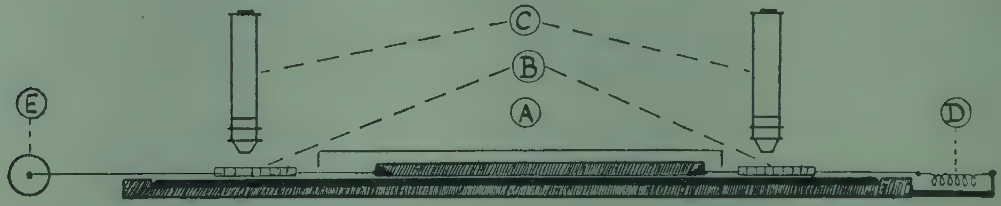

FIG. 1. Diagram of extensimeter, employed by Schofield & Scott Blair and by Halton & Scott Blair.

A dough cylinder A is floated in a mercury bath and protected by a cover to prevent drying of the dough surface. Two small graduated scales B, which are observed through microscopes C, are attached at the ends of the dough by means of very fine cotton threads. To the scale on the right is fastened a steel spring D (originally a rubber strand) which has been calibrated by hanging weights on it. The other scale is connected by cotton to a small winch E, which can be wound either by hand or by a small motor. By winding up the winch the dough and the scales move to the left. The position of the scale on the right can be used as a direct indication of the stress applied to the dough. The value of the stress is proportional to the extension of the spring and inversely proportional to the cross-section of the dough cylinder.

Studying the influence of varying conditions of stress and strain with the extensimeter, viscosity appeared to depend not only upon the shearing stress, but also upon the amount of shear. Actually viscosity decreases with increasing stress and increases with increasing strain, phenomena similar to structural viscosity and work-hardening. The gasretaining capacity of a dough during fermentation depends among other things, on this work-hardening. Because of these effects it will be necessary to specify the conditions of stress and strain, under which viscosity measurements are made.

A more direct method was used by Schofield and Scott Blair to determine the dependence of viscosity on the shearing stress and the extent of shearing, by studying the rate of elongation of cylinders of unyeasted dough hung vertically by their upper ends and allowed to extend under the action of gravity (the method of "rheograms"). They found a satisfactory agreement, so far as order of magnitude is concerned, between the viscosities obtained directly in this way and those calculated as the product of relaxation time and modulus. Quantitative discrepancies, however, were observed. Further investigations with a modification of the mercury bath apparatus revealed that dough shows two other effects in addition to structural viscosity and work-hardening, namely elastic after-effect and elastic hysteresis. Both these properties being characteristic of metals and other systems.

The existence of the elastic after-effect, due to inhibition of elastic recovery caused by viscous resistances in the dough, means that certain deformations will be regarded as plastic which are in reality elastic, unless sufficient time is given for recovery. Considerable errors in the correct determination of viscosity and modulus would then be due to this effect. Elastic hysteresis was shown to cause variations in the modulus of the dough. The modulus decreases steadily when the stress is raised or lowered, but increases abruptly to a considerable extent at each point where the sense of the stress change alters.

Taking these effects into consideration and using the value of the modulus most applicable to the conditions of stress relaxation, the discrepancies between viscosities calculated from relaxation times and those obtained from rheograms disappeared and the results of both methods now fell in line.

According to Schofield and Scott Blair the behaviour of flour dough under stress can be described by the expression

$$\frac{de}{dt} = \left(\frac{1}{n} \cdot \frac{d\tau}{dt} - \frac{da}{dt}\right) + \frac{1}{\eta} \cdot \tau$$

which is the Maxwellian equation for expressing the rate of elongation, with the addition of a term da/dt, in which a represents the influence of the elastic after-effect.

de/dt = rate of elongation of the dough cylinder
τ = shearing stress
n = shear modulus
η = viscosity.

The term da/dt is small during the application of stress and it may be assumed that α tends to zero as a steady condition is approached when the system is left undisturbed. The term is large when abrupt changes of stress have recently occurred. α as well as the modulus do not appear to depend on the absolute value of the shearing stress, unlike the viscosity, which is extremely sensitive to the absolute value of τ.

In continuation of these studies HALTON & SCOTT BLAIR [1936a, b, 1937] investigated the relations existing between certain physical constants of a dough and its baking quality. Use was made of a modified and improved form of the previously mentioned mercury bath extensimeter, by means of which both viscosity and modulus can be measured in one experiment. The importance of a carefully standardized method is emphasized by the authors, since mixing time and rest periods have a marked influence on the viscosity and modulus of the dough, whereas the force applied in extending a dough cylinder from a metal gun largely affects the physical properties of the prepared dough cylinder. Temperature control also appeared to be essential since viscosity and modulus were found to fall by about 10 % and 5 % respectively with a rise in temperature of 1° C. Hence the ratio of viscosity to modulus (relaxation time) is lowered by increasing temperature.

Experiments with flours of different strength [1]), carried out in order to investigate the connection between water content of the dough and its viscosity and modulus, revealed that both viscosity and modulus fell with increasing water content, the relative effects on these two properties, however, not being the same. In the case of a strong flour the effect of varying water content on viscosity and modulus appeared to be less than with a weak flour. At a water content corresponding with the normal bakehouse absorption, the doughs exhibited nearly similar values for the modulus, whereas they differed considerably in viscosity. Halton and Scott Blair, therefore, used a constant mean value of the modulus when comparing the physical properties of doughs, made from different flours.

Under these conditions a dough made from a strong flour has a far greater viscosity than a dough made from a weak flour. On the other hand the modulus of the strong flour dough is much lower than that of the weak flour dough, when the doughs are compared at the same viscosity.

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[1]) Flour strength could be described as the capacity of a flour to make big, well-piled loaves and is closely connected with a high percentage of gluten of good quality (SCOTT [1951, p. 20]).

In determining the effect of fermentation on viscosity and modulus it was found that both properties fell with time of fermentation, viscosity falling more rapidly than the modulus. The initial viscosity was highest and the decrease in viscosity smallest with the strong flour, whereas the ratio of viscosity to modulus was highest throughout the time of fermentation. The weak flour exhibited a low initial viscosity, a low viscosity/modulus ratio and a considerable fall in both with time. Thus increase in water content and ageing both affect viscosity and modulus in the same manner.

Yeast appeared to have but small effect on viscosity and modulus.

These experiments led Halton and Scott Blair to conclude that viscosity and modulus are of major importance. A substantial elastic expansion under the relative low gas pressure within a fermenting dough requires a low modulus. Viscosity, on the other hand, must be high enough to prevent an undesirable flowing out of the dough under its own weight. The ratio of these two properties (relaxation time) therefore appears to be the most important single criterion of baking quality.

Since neither viscosity nor modulus is constant, relaxation time is not a constant. However, viscosity and modulus are not independent variables, since it has been found later by HALTON [1938] that the ratio viscosity/(modulus)^x is constant for any particular flour, the numerical value of x varying between 1.8 and 2.0. This indicates that in spite of the differential effect of water content and age on viscosity and modulus, there exists some relationship between these properties irrespective of the condition of the dough. Halton suggests the use of this ratio for evaluating flour strength.

As both viscosity and modulus are affected in the same way by changing water content, an increase in water content has the undesirable effect of lowering the viscosity, but the beneficial effect of decreasing the modulus. On the other hand a decrease in water content is desirable in connection with viscosity, but undesirable in connection with modulus. Thus, the optimum amount of water (or "water absorption") is determined by the optimum balance between viscosity and modulus.

In the bakehouse much attention is paid to two dough properties in connection with the judgment of baking quality, namely "spring" and "shortness". It is of interest in this connection to remark that spring, i.e. the recovery of the dough after deformation and shortness, i.e. the tendency to tear, are dough properties which are judged by feel. D. KATZ [1937] and SCOTT BLAIR [1939] made a study of the psychological aspects of assessing physical properties of dough by touch and from their observations it appeared that the baker's judgment is based on the general behaviour of the dough and not on the separate viscous and elastic properties. To quote Katz: "the psychological properties e.g. body and spring do not correspond to the physical properties of viscosity, elasticity etc., but are rather the result of a complicated co-operation of the different senses of the skin, the muscles, the sinews and the joints".

Changes in elasticity seem to be better differentiated by touch than those in viscosity, but on the whole the subjective impressions of the baker are inferior to the physicist's objective methods of testing dough properties. It is therefore rather difficult to express the psychological properties, spring and shortness, in terms of definite physical constants.

According to Halton and Scott Blair, spring is considered to be associated with both viscosity and modulus. That is, a dough having good spring will have a relatively high viscosity and low modulus (high viscosity/modulus ratio or large relaxation time) whereas a dough showing bad spring will have a low viscosity and high modulus (low value for viscosity/modulus ratio).

Shortness, as determined by the baker, is a function of both ductility and tensile strength, ductility representing the critical deformation of the material at the point of rupture and tensile strength the critical stress. Shortness is affected as well by work-hardening as by structural viscosity. Following the relationship between structural viscosity and the brittleness of materials, the same authors developed a method for assessing shortness and a fair correlation between shortness and structural viscosity was found.

Thus spring and shortness, both important factors for the judgment by the baker, appear to be connected with relaxation time and structural viscosity. It is realized, however, that tensile strength, determining the extensibility of the dough, is also a factor of major importance.

In an attempt to explain theoretically the change in properties when dough is extended, Halton and Scott Blair assume that a progressive slippage and breaking of junctions take place between the fibers, which are formed during the extension (This formation of a more or less fibrous structure can easily be observed when dough is extended until it breaks).

This concept of slippage and breaking under increasing stress was further developed by SCHOFIELD & SCOTT BLAIR [1937a], who demonstrated the general nature of the process by means of a mechanical model, consisting of six springs, shown in Fig. 2. Three of these springs are securely linked at P, the other three at Q. In R, S and T they are insecurely linked in pairs, while the springs linked in S are only half the length of the others. If the links at R, S and T will stand the same maximum stress, the link at S will break before those at R and T. On applying a small stress all the links will hold (Fig. b) and the system will return to the original condition (Fig. a). If sufficient stress is applied to break the link at S (Fig. c), the system will return only to the condition shown in Fig. d. Permanent elongation results and the system has therefore "flowed".

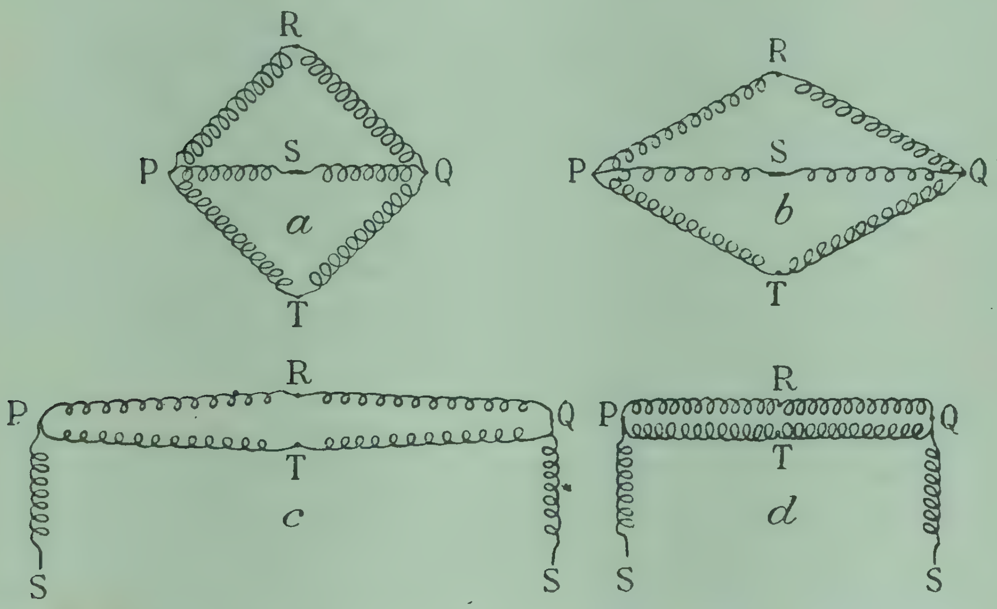

FIG. 2. Model of a system of six springs (SCHOFIELD & SCOTT BLAIR [1937a]).

In flour dough, where many of such systems exist, the picture is more complicated. When stress is applied, a progressive breaking of individual junctions will take place, but the stress needed to effect any further breaking of junctions must be the higher, the greater, the number of junctions already broken. It is clear that the phenomenon of work-hardening is produced by this progressive breaking of junctions.

Further experiments with strips of washed gluten revealed a close resemblance between the behaviour of the dough and of the gluten. Schofield and Scott Blair therefore assume that the gluten in the dough is mainly responsible for the observed properties. Accordingly they believe that the gluten builds up an elastic network, which largely determines the mechanical behaviour of flour dough. It is suggested that the branched protein chains of the gluten act as the securely fastened springs in the mechanical model, the insecure links being formed by electrostatic attraction between oppositely charged groups.

Summarizing, the following picture of the behaviour and structure of dough results from the fundamental investigations so far described:

(1) Two dough properties are of chief importance, namely viscosity and modulus.

(2) Both properties depend on the magnitude of stress and strain and vary with temperature, age and water/content of the dough.

(3) Maxwell's concept of time of relaxation (viscosity/modulus) can be extended to cover dough behaviour.

(4) Flour dough exhibits the phenomena of structural viscosity, work-hardening, elastic after-effect and elastic hysteresis.

(5) The "spring" of a dough depends on relaxation time, whereas the "shortness" of dough is connected with structural viscosity. Baking quality primarily depends on these two factors, i.e. relaxation time should be high and structural viscosity should not be too great.

(6) The branched protein chains of the gluten form a continuous elastic network, the linkages between these chains not being equally strong at all points.

Later, HALTON [1949a, b] continued the fundamental work on physical dough properties and new light was thrown on those aspects which still remained obscure.

Earlier it had been found that optimum water content is closely connected with a definite value of the modulus. Later experiments showed that the rate of extrusion of dough through an orifice was determined not by the viscosity but by the modulus of the dough. Halton used these findings for devising an apparatus by which the rate of extrusion of dough through an orifice under constant pressure could be measured, (HALTON & FISHER [1939]). With this instrument the absorptions of different flours can be assessed by determining the proportions of water required to give the extrusion time, which is known to correspond to the desired modulus. The same principle for determining water absorption was used by STAMBERG & BAILEY [1940].

Halton also constructed another instrument by means of which the dough can be stretched mechanically and the stress-strain relationships are automatically recorded.

> A ball of yeasted dough, prepared under strictly defined conditions, is impaled on two pegs. The bottom peg is moved downwards at a constant rate by means of a motor and the dough is stretched. The force exerted by the dough upon the upper peg, which is attached to a balance, causes this peg to move downwards, the degree of movement being proportional to the force. This movement is recorded upon a moving chart.

In the load-extension curves thus obtained from doughs made to have the same modulus, the height of the curve appeared to be proportional to the relaxation time, the length to the extensibility and the area under the curve to the tensile strength of the dough.

A typical example of load-extension curves of two different flours is given in Fig. 3.

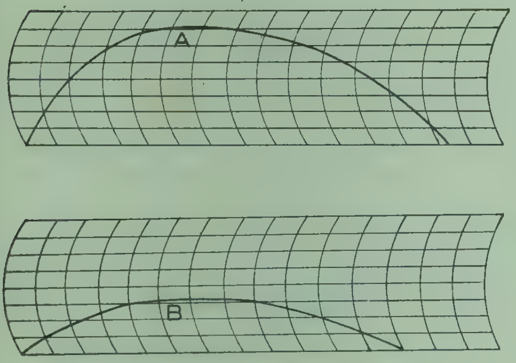

FIG. 3. Extensometer curves.
Curve A : dough with high viscosity/modulus ratio and good extensibility (excellent baking quality);
Curve B : dough with poor viscosity/modulus ratio and fairly good extensibility (unsatisfactory baking quality).

It has previously been shown that a dough softens with age, the change in the ratio of viscosity to modulus being the same as that resulting from an increase in the water content of the dough. Allowance for this softening was now made in the experiments by adjusting the water contents of the doughs in such a way that they have the same extrusion time when the dough is baked or tested on the extensometer.

The effect of age on the shape of the extensometer curves of non-yeasted and yeasted doughs appeared to be different, whereas the effect on extrusion times was the same. In the case of the non-yeasted dough the changes in the load-extension curves, — decrease in height and increase in length — and the fall in extrusion time suggest a softening of the dough, due to an increase in the free water content. With a yeasted dough, the product of height × length of the extensometer curve and the extrusion times also decrease with age, but the height of the curve increases and the length decreases, suggesting, by contrast, that the dough becomes tighter and not softer. In explaining these conflicting data, the author points out that the stretching process modifies the physical characteristics of the dough. Stretching tests normally give rise to work-hardening and hence the shape of the curves obtained depends on the condition of the dough as well as on the response to stretching. It is suggested by Halton that in the case of a yeasted dough, the changes in dough properties, accompanying fermentation, and in addition the continuous stretching by the gas generated, result in an increasing work-hardening of the dough when it is stretched. This work-hardening toughens the dough, which is reflected in an increasing height of the load-extension curve. By the progressive breaking of links in the protein network the dough becomes more brittle and the extensibility decreases, resulting in a decrease in the length of the curve.

As stated by Halton, these differences between non-yeasted and yeasted doughs may be partly due to the biochemical and chemical processes taking place during fermentation. In view of the recent investigations of ERSTADT [1950, 1952], it may be of interest to give special attention in further research to this side of the problem.

Experiments with the extensometer have further shown that bread quality is a function of tensile strength and relaxation time, tensile strength being the basis of potential flour strength and relaxation time being a measure of the condition of the dough. Normal fermentation, flour improvers or mechanical manipulation of the dough did not appear to affect tensile strength. Relaxation time, however, is considerably modified by the diverse chemical and physical processes in breadmaking as well as by the use of flour improvers.

Several other dough stretching instruments have been used by different investigators for measuring the rheological properties of flour doughs. Among them mention may be made of the stress-meter of BOHN & BAILEY [1936a, b, 1937], who studied stress-strain relationships on stretching a dough cylinder to five times its original length. Dough gun and mercury bath were similar to those devised by Schofield and Scott Blair, but the stress on the test-piece was registered on a stress-balance and measured directly in grams. After extension, the decay of stress with time was noted by taking periodical stress readings. Strong flours appeared to give higher stress readings than weak flours. Following this observation, Bohn and Bailey investigated the possibility of using the stress readings as an index of baking quality. A significant correlation was only found, however, between stress readings and the ability of a flour to withstand excessive mixing or severe handling. Increase of temperature and water content of the dough, as well as fermentation, decreased the stress readings.

The fundamental nature of dough behaviour, however, was not investigated by these authors and from the foregoing it will be clear that single stress values cannot alone describe behaviour or evaluate baking value.

Issoglio [1937] and Sauer [1936a, b, 1937] have also studied the physical properties of dough by stretching dough cylinders on a bath of mercury, the former at a constant temperature of 20° C, the latter at 30° C. From the data of his experiments Issoglio calculated modulus and viscosity of the dough. Sauer did not express his results in absolute units. The fall in stress when a piece of dough is extended and held extended for varying times was used as a criterion of internal viscosity. In agreement with Scott Blair *et al.* Sauer observed a fall in modulus with time.

The modulus of elasticity or Young's modulus was calculated from dough stretching experiments by Levi [1950], who determined the stress built up in a thin cylinder of dough when deformation was increased. Kneading for 10 minutes increased, but kneading for 15 minutes again lowered Young's modulus.

So far, no special attention has been given to the starch of the flour. In former days investigators held the view that the starch in flour dough merely acted as a filler and a substrate for amylase activity. The early work on the rheologically simpler dilute flour-water suspensions, in which starch appeared to be of no importance, probably gave rise to this view. In dough, however, the starch/water ratio is quite different from that in flour/water suspensions and it is highly doubtful if conclusions from experiments with flour suspensions hold for dough. Later, it appeared that on the whole the rheological properties of flour dough show a closer resemblance to those of starch pastes than to those of flour-water suspensions (SCOTT BLAIR [1940]). See also Chap. I.

In 1937 it was emphasized by MARKLEY [1937], who demonstrated the thixotropic nature of the starch-water system, that starch is an important factor in determining dough viscosity and that "starch can no longer be ignored in the interpretation of physical observations made upon bread doughs". The influence of starch on the elastic properties becomes obvious, when comparing the rates of elastic recovery of dough and of gluten washed from the dough. Dough appears to recover considerably more slowly than gluten, the only difference between these two materials being the presence of starch in the dough.

SCHOFIELD & SCOTT BLAIR in their studies on dough properties [1932b, 1937a, b] point out that, due to the anomalous viscosity of starch paste, dough behaviour is influenced by the starch to a greater extent at low than at high stresses. Experiments on dough stretching under smaller loads revealed that, in the range where no flow takes place, dough shows an elastic fatigue on repeated loading. On the other hand it can be considered as a type of thixotropic behaviour since the modulus rises rather rapidly on resting. Furthermore the process is complicated by the phenomenon of work-hardening, since the modulus seems to increase rapidly as soon as the least flow takes place. Finally, evidence has been obtained that the starch paste, which permeates the gluten network, has a yield-value. The existence of elastic hysteresis is thus found even when the load on the dough is changed so slowly that elastic after-effects are avoided. The existence of a yield-value was also found by VOLAROVICH & SAMARINA [1935] who used a rotation viscometer in studying the plastic properties of dough.

HALTON [1938] suggests that the softening of a dough with age is due to a decrease in viscosity of the starch paste, caused by "syneresis" of the gluten. Although proteins have a greater water-binding power than starch, they are not able to hold all the initially bound water and water is partially released. This released water dilutes the starch paste, thus reducing its viscosity.

The importance of the starch in connection with dough properties and bread characteristics becomes even more apparent when comparing wheat flour with rye flour. The elastic properties of a wheaten flour dough are ascribed to the gluten, which can easily be washed out from the flour by simple manipulation. In the case of rye flour, however, one does not obtain a coherent elastic gluten mass when washing out in the same way and here the starch fraction plays a prominent role in determining baking quality, in particular the viscosity of the starch paste (BRABENDER [1937]).

Since rye flour is used to a far greater extent for breadmaking purposes in Germany and the Scandinavian countries than in Western Europe, Britain and the U.S.A., much attention has been given by investigators from these countries to the characteristics of rye flour. Their investigations, however, deal mainly with gelatinization and viscometric studies of rye-flour suspensions (BRABENDER, MUELLER & KÖSTER [1937], SCHMIDT & SCHOLZ [1938], BIÉCHY [1935, 1938], SCHULERUD [1934]). Fundamental work has so far not been carried out on the rheological properties of rye-flour dough.

The connection between starch properties and the crumb characteristics of rye bread probably gave rise to the view expressed by ROTSCH [1949, 1951] that, even in wheat flour, the starch is much more important for the building up of a network structure than the gluten. Although this seems an overestimation of the role of starch, recent investigations by HESS [1952] and HANSSEN [1952] seem to indicate that, dependent on the circumstances and the type of flour used, a certain network-building function must be ascribed to the starch. The swelling and the partial gelatinization of the starch under the action of heat during baking thus become more important in connection with the ultimate fixation of the crumb structure.

Since the rheological properties of starch pastes, including swelling and gelatinization, are described in detail by Hofstee and de Willigen (Chap. I), the reader is referred, for further information on this point, to their chapter.

3. Theory of the Rheology Involved in Breadmaking

Some fundamental properties of dough having now been discussed, it is proposed to deal in this section with the theoretical background of the rheological phenomena involved. This will be done separately for the different stages of the breadmaking process.

3. 1. *The Mixing Process*

By mixing together flour and water into a dough, the water is partially bound by the starch and proteins by means of capillary forces

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and chemical bonding. The remaining portion exists in a free state and is available as a solvent for different soluble substances present in the flour. The molecules of water next to the hydrophylic surfaces of the starch granules and protein molecules are held so strongly that they have no freedom of motion. The layers superimposed upon these films have more and more freedom until the water molecules have practically the freedom which exists in bulk water. Too much freedom results in a slack dough; too little freedom in a stiff dough. Since no sharp distinction can be drawn between free and bound water, an exact calculation of the amounts of water occurring in both states can hardly be made. SKOVHOLT & BAILEY [1935b] and VAIL & BAILEY [1940] showed that from one-half to two-thirds of the water is bound. SWANSON [1946, p. 111] estimated that one-third of the water in dough has the same freedom as in bulk water. KUHLMAN & GOLOSSOWA [1936] reported that the solids in flour bind 44 % of their weight of water and BAKER *et al.* [1946] found that 100 g of dry flour bind 27.3 g of water.

The internal friction in the outer layers of water molecules determines to a large extent the viscosity of the dough and depends, among other things, on the thickness of the layers, the temperature and the concentration of soluble solids. Since variations in the amount of water used in making a dough mainly affect the amount of free water, it is obvious that differences in water content manifest themselves in differences in dough viscosity. On the other hand, the amount of bound water depends on the nature and extent of the adsorbing surface, which influences the thickness of the layers of water molecules. Protein molecules are characterized by a large surface in proportion to their mass. Hence, a dough made from flour with a high protein content will have a higher viscosity than a dough made with the same amount of water from a flour with a low protein content. Furthermore the physical properties of the proteins, in practice called "the quality of the proteins", and the size of the flour granules also influence dough viscosity.

Dough viscosity or mobility is thus dependent upon many factors and it will be clear that the amount of water giving optimum results, varies with any particular lot of flour. As stated by HALTON [1938] and MARKLEY & BAILEY [1938a] the term "absorption" should be used to denote *this* amount of water, i.e. the proportion of water in flour which results in dough (and bread) of optimum quality.

Water absorption appears to be, to some extent, a compromise between high viscosity and low modulus as mentioned before in II, 2, while absorption is closely connected with a definite modulus.

The mixing of wheat flour with water results in a swelling of the proteins and the formation of gluten, the most characteristic ingredient in dough. The gluten particles assume a fibrillar or laminar form and in the early stages of mixing they are arranged in a heterogeneous pattern. As mixing continues this pattern is changed into a more or less parallel one and ultimately a continuous three dimensional mesh-network results. The formation of this network is usually referred to as the "development" of the dough. Optimum development manifests itself in the dough's assuming a smooth appearance, a "drying up" as the baker terms it, and in a maximum viscosity or minimum mobility of the dough.

From the work of Markley [1938] and Stamberg [1939] it appears that a minimum protein content of about 7.5 % is required for the building up of a complete gluten network. Below this level the physical characteristics of the dough change to those of a starch paste. Above this percentage, the thickness of the protein film increases with higher protein content and the time to reach minimum dough mobility increases in an almost linear fashion. Apart from the quantity, the quality of the proteins also determines the time required for optimum development: e.g., doughs made from strong flours require more work for optimum development than do medium strength or weak flour doughs (Bohn & Bailey [1936b], Stamberg & Bailey [1938]).

The time required to mix a dough to optimum development depends on the speed of the mixer arms, the temperature, the strength of the flour, the rate of hydration of the flour particles and on the dough ingredients used. On the whole, a medium speed mixer has some advantages over a high speed mixer. In the case of the latter, mixing time must be carefully adjusted in order to prevent overmixing, which may occur easily especially with weaker flours.

If mixing is continued beyond the stage of optimum development or minimum dough mobility, the dough tends to slacken and a rather rapid increase in dough mobility takes place, indicating a physical breakdown of the dough. This increase in mobility has been studied by many investigators, but what actually happens is not yet fully understood. A division of the protein aggregates may occur (Skovholt & Bailey [1935a]), or a breaking of the gluten fibrils by the continuous stretching, or a plastic displacement (Swanson [1936, 1939]).

In this way the gluten fibrils become very attenuated and possibly this is one reason why gluten cannot be washed out in the usual way from an overmixed dough. Some mechanical degradation of the gluten structure thus seems to take place. However, if overmixing has not been carried too far and the dough is allowed a rest period, it then becomes possible to remove again the starch from the gluten by the ordinary washing process. Apparently the separated and attenuated gluten filaments come together, forming larger strands and the dough goes back more or less to the condition which existed before overmixing took place. The recovered structure is probably different, however, from the original. Such a recovery does not take place in the case of extreme overmixing. Viscosity and modulus are considerably lowered by excessive mixing, but they increase on resting, whereas the tensile strength of the dough is permanently lowered.

The drastic alterations in physical dough properties caused by extended mixing cannot be fully accounted for by protein decomposition, nor the slackness of an overmixed dough by an appreciable change in the percentage of bound water. Some increase in solute concentration in doughs has been noted and this may be associated with changes in dough viscosity (SKOVHOLT & BAILEY [1935a, b]). Many other factors have been shown to influence the rate of increase in dough mobility. Apart from the more mechanical effects, such as the speed of the mixer arms and the type of mixer used, flour strength (BRABENDER [1932]), the action of amylolytic enzymes (MUNZ & BAILEY [1937]), proteolytic enzymes (LANDIS [1935]), the thixotropic nature of the starch/water system of the dough (MARKLEY [1937]) and the action of certain oxidizing and reducing substances such as bromate, cysteine and glutathione, contribute to the change in mobility upon prolonged mixing. Glutathione has been found by JØRGENSEN [1936] to accelerate the increase in mobility to a very great extent.

The interpretation of the rate at which dough mobility increases thus becomes very difficult and MARKLEY & BAILEY [1938b] conclude that the changes in viscosity do not provide a direct measure of flour strength or gluten quality.

Finally one aspect of the mixing process must be mentioned briefly, namely the relation of mixing to the origin of the gas cell in dough. The work of BAKER & MIZE [1941, 1946] and of BAKER [1941] shows that incorporation of air does not proceed at an even rate during the mixing period. The air beaten in during the early stage of mixing is of practically no consequence as a source of gas cells. An undermixed dough contains only a small number of them. In the latter stage of the mixing process, near the point where dough viscosity is highest, gas occlusion takes place at a most rapid rate. Evidence has been obtained that the fine cell structure is acquired by gas subdivision, producing cells of small size, and not by gas occlusion. BURHANS & CLAPP [1942] on the contrary, assume that the fermentative action of yeast is largely responsible for the origin and formation of the cell structure of dough.

3. 2. *Fermentation*

The fermentation process is even more complex than the mixing process, since so many factors are acting together. An adequate review of all these factors is not possible within the space available and only those factors which are important from the rheological point of view will be discussed.

The main purpose of fermenting a dough is to generate sufficient gas for maximum aeration and to disperse properly the colloidal structure of the dough so that a maximum amount of gas will be retained (CLARK [1938]). By the action of the yeast cells on the available sugars, carbon dioxide gas and alcohol are formed, and the fibrous gluten network is stretched. The thin gluten walls of this network and the water film covering these walls form a membrane, which is able to retain the main portion of the gas produced. A marked increase in dough volume results and the dough assumes a light and spongy character. The extensibility of the gluten allows for this expansion, while the elasticity of the gluten at the same time prevents a too easy expansion. After an initial rise, usually to the limit of extensibility, the dough is worked down. By these mechanical actions of stretching and pulling together, the gluten strands come into a more attenuated condition and the subsequent rise will take place correspondingly faster. By dividing, proofing and moulding, the gluten strands are again stretched and pulled together, the total effect of these operations being a dough condition in which a larger volume and a finer texture is ultimately possible. After panning, the dough piece is aerated again in the final proof after which it is placed in the oven.

It has long been known that, as fermentation proceeds, definite changes in the physical character of the dough take place.These changes are usually collectively referred to as the ripening of the dough. One of the principal alterations is a mellowing or softening of the gluten so that it is capable of forming thin gas-retaining walls. These membranes must not be too strong or too weak. Several hypotheses have been advanced to account for this important change, but what actually happens is not yet clearly understood. The following factors have been suggested as a possible basis for an explanation: the action of yeast and of enzymes, particularly the action of proteolytic enzymes in the yeast and the flour on the gluten proteins (SHARP & GORTNER [1924], BROWNLEE & BAILEY [1930], RUPP & BAILEY [1937]); the influence of the alcohol produced during fermentation (JOHNSON & BAILEY [1925]); the influence of the acids formed (JESSEN–HANSEN [1911]) by which the hydrogen ion concentration is altered, which in turn affects the physical properties of the gluten; the action of substances such as phosphatides (WORKING [1928]); and finally the mechanical stretching of the gluten caused by the expanding gas bubbles, followed by a packing together when the dough is worked down (SWANSON & WORKING [1926]). Some authors state that no actual chemical change of the gluten proteins takes place (BROWNLEE & BAILEY [1930]) while others (SAMUELS [1935], AMOS [1931]) have shown that in a fermenting dough the slow but progressive liberation of amino nitrogen, which is noticeable in non-yeasted dough, is masked because of the yeast metabolism in which the liberated nitrogen is utilised. It was pointed out by Amos that, although the change in chemical constitution is only slight, it may be accompanied by a relatively large alteration in physical properties. The work of SKOVHOLT & BAILEY [1935a], BALLS & HALE [1936a, b] and RUPP & BAILEY [1937] supports this view. Recently ERSTADT [1950, 1952] has put forward the hypothesis of both a breaking and restoring of hydrogen bonds between the protein chains. It is not impossible that these processes contribute to the change in dough properties during fermentation.

Practically all the factors enumerated influence favourably the ability of the gluten to form thin membrane walls, which are of the utmost importance for the ultimate porous structure, while at the same time the extensibility and elasticity is retained.

As early as 1925 SWANSON [1925] stated that the properties of this particular cell wall structure are due to the glutinous network of strands. Dough cells are formed as soon as evolution of gas begins. The surface properties of the water, covering the starch and protein structure, render these cell walls gas-tight and an increase in volume is made possible by the elastic properties of the protein strands. The cells will coalesce when the elastic limit is reached.

BAKER [1941] studied the structure of the gas cell and from his work it appeared that in a developed dough the wall of the gas bubbles is essentially glutinous in character. The mechanism of expanding is described by this author as follows:

> "The dough forms a matrix of glutinous and starch material from which the wall draws the required amount of gluten into its expanding surface by the strength of its elastic properties, producing a gas-tight film on the inner surface of the bubble. In case the gluten does not have sufficient strength to accomplish this result it breaks and expansion of the bubble no longer continues. The properties of the bubble are largely determined by those properties of the gluten which enable it to retain its integrity as a film at the inner bubble surface. If the gluten itself has a relatively low viscosity and hence is somewhat fluid in character, it will break rather than pull more of the glutinous material into the film. Yet, in order to flow from the matrix the gluten must still be somewhat liquid in nature, but also tenacious. This tenacity is obtained because its viscosity is relatively high in comparison to its modulus of elasticity, whereas the flow may be obtained because the numerical values of the viscosity and elasticity are low. A further condition in the dough that may affect the travel of gluten from the matrix into the surface film is affinity or adhesion between the starch granules and the flowing glutinous material".

The changes in dough characteristics during fermentation, expressed in rheological terms, are a decrease in extensibility which is accompanied by an increase in work-hardening when the dough is stretched (HALTON [1949a, b]). This increased work-hardening raises the viscosity and, since the modulus is hardly affected during stretching, the relaxation time also increases, resulting in improved bread quality. A correctly fermented dough shows good response to the stretching action of moulding, the dough becoming more elastic. After moulding, the dough relaxes slowly. Doughs made from flours with high protein content generally work-harden considerably on stretching and relax slowly afterwards, whereas doughs made from flours with low protein content work-harden less and relax more quickly. The balance between work-hardening and relaxing determines the final condition of the dough when it goes to the oven.

It is common practice to add certain chemicals to the flour to improve bread quality. Potassium bromate and persulphate as well as gaseous nitrogen trichloride and chlorine dioxide are well-known flour improvers. The mechanism of improvers such as bromate has aroused great interest and two contradictary theories (JØRGENSEN [1935, 1936, 1939], SULLIVAN *et al.* [1940]) have been advanced to explain the improving effect. These theories will not be discussed here, but it is of interest to mention the influence of such improvers on the rheological properties of dough. The general effect appeared to be an increase in height and a decrease in length of the Halton Extensometer curves with increasing proportion of improvers. This indicates that the dough has more spring and is less extensible, the effect being the same as that resulting from fermentation. The product of height × length appeared to be more or less constant. This is of special interest because experiments have shown that this product is greater the stronger the flour, which means that flour strength is determined by the tensile strength of the dough. Therefore the significance of the constant product is that these improvers do not influence the strength of the flour, but rather produce an optimum balance between the individual dough properties. The product decreases if chemical treatment or fermentation is carried too far and bread quality is impaired because the tensile strength of the dough is lowered.

3. 3. *The Baking Process*

By the application of heat during the baking process the dough mass is transformed into a light, porous palatable product.

As soon as the dough is placed in the oven, the immediate effect of heat is the formation of a thin film on the dough surface, this film being extensible to an extent depending upon the moisture condition in the oven. Secondly, a rapid increase in the total volume of the gases takes place which results in an expansion of the dough, the so-called oven spring. Oven spring is determined by the increase in volume of gas and by the amount of gas which is retained. It is essential for good oven spring that the protein network should stand the pronounced strain resulting from gas expansion without rupturing. The softening of the dough during heating further facilitates oven spring. STAMBERG & BAILEY [1938] have found a certain relationship between oven spring and mixing time, most doughs showing increased oven spring with increased mixing until a highly overmixed condition is reached when oven spring starts to decrease. This behaviour is undoubtedly related to the condition of the gluten.

During the softening of the dough, sufficient viscosity and elastic extension must be retained until the starch swelling increases the strength of the dough structure. Starch swelling is accompanied by a transfer of water from the other dough ingredients to the starch granules, thereby partly dehydrating the gluten. The strength of the gluten strands is increased by this process and the fibers become more viscous and elastic. Oven spring continues during and after primary starch swelling and finally ceases during the coagulation of the gluten. The plastic and elastic expansion of the dough thus continues after starch swelling has started to alter the dough characteristics to an appreciable extent.

In the period between the beginning of starch swelling and the coagulation of the gluten the temperature of the dough reaches a level where enzymic action is inhibited. As heating continues, dough mobility markedly decreases, especially between 62 and 67° C (BAILEY & MUNZ [1938]) and finally the dough assumes a more or less rigid state caused by the coagulation of the proteins and the partially gelatinized starch.

During the first half of the baking process the heat has a liquefying effect on the gluten and the starch here comes in as a factor in maintaining the structure and the volume of the dough (SELMAN & SUMNER [1947]). At this point the viscosity of the starch gel becomes important for the expansion of the dough. Optimum expansion becomes impossible when the viscosity of the starch gel is too high, leading to an unsatisfactory volume and texture of the loaf. On the other hand the dough is not able to stand the increasing gas pressure if the viscosity is too low, and this results in a coalescing of small gas cells into larger ones and again in a diminution of volume.

The viscosity of the starch gel is to a large extent determined by the enzymic action of alpha-amylase, since this enzyme exerts a liquefying action on starch (HOLLENBECK & BLISH [1941]). ANKER & GEDDES [1944] showed that the gelatinization temperature of wheat flour suspensions and the maximum viscosity reached during gelatinization are decreased by alpha-amylase. The relationship between alpha-amylase content and starch–gel viscosity in the dough now becomes apparent. A flour deficient in amylase will yield a dough in which the viscosity of the starch gel is too high: a flour with excessive amylase activity leads to a low viscosity of the starch gel in the dough. In both cases bread quality is impaired while in the latter case a more or less damp and even sticky bread crumb is obtained. KOSMIN [1936, p. 125] points out that the sticky crumb is due to the dextrinogenic action of the enzyme, which leaves unsufficient unconverted starch to bind all the water at the time of gelatinization.

Obviously a proper balance between starch gelatinization and alpha-amylase content is necessary in order to obtain bread of optimal crumb properties. In particular an appropriate level of alpha-amylase activity exerts a beneficial effect on the texture and tenderness of the crumb. The most important action of the alpha-amylase takes place at high temperatures in the initial stage of baking, but the enzyme also conditions the starch during fermentation.

The reactions occurring during the baking of dough were studied by BAKER & MIZE [1939a, b], who made use of a special apparatus for testing doughs described by BAKER [1939], by means of which crustless bread was produced by heating the dough internally. Their findings are of particular interest in connection with the changes in dough, due to the swelling of the starch and the pressure built up by the gas generated. As a result of the swelling of the starch, the force required to stretch the dough increases, elasticity and viscosity of the gluten increase by the transfer of water from the gluten to the starch and the location of the starch granules in the dough mass becomes fixed by their increased volume. Further rearrangement of these granules occurs only with difficulty and continued expansion of the dough now depends mainly on an increased elastic extension of the gluten. Meanwhile the dough film, forming the walls of the gas cells, become thinner as oven spring proceeds and as soon as the tensile strength of the membrane is exceeded, as a result of the increasing pressure the bubbles break. This causes a fall in pressure and a decrease in the rate of oven spring. The earlier this rupturing, the lower the oven spring and the smaller the bread volume.

Elastic extensibility and tensile strength thus appear to be the physical properties which mainly govern the condition of the dough during baking.

Experiments have further shown that a high initial pressure and a rise in pressure during baking are desirable. The texture of the bread will be increasingly better the steeper the slope and the longer the duration of the pressure rise. The slope of the pressure curve is controlled by the ratio of viscosity to modulus, a steeper slope corresponding with a higher viscosity. Pressure does not usually rise continuously during heating. A drop occurs during the starch swelling and at the end of the baking period.

It has also been shown that the dough is at its minimum viscosity prior to and during the early stages of starch swelling and that the condition of the dough at this stage is optimal for the coalescence of the gas bubbles. An interesting feature is that oven spring, notwithstanding a drop in pressure, does not fall abruptly. This indicates that no complete loss of the gas occurs. It is believed that gas bubbles break and coalesce to form fewer and larger ones. As less surface is required to hold the same amount of gas in one bubble than in two, the stress on the surrounding dough film decreases and pressure falls. A drop in pressure is therefore not necessarily accompanied by excessive loss of gas but leads to a loss in texture of the bread. With unoxidized flours such a drop in pressure is quite pronounced, resulting in a bread with an uneven grain and having relatively large cells. In oxidized doughs the pressure rises more continuously. Evidence has been obtained that the action of potassium bromate is to increase the pressure and maintain a continuous pressure rise. Oxidation has apparently raised the viscosity of the dough (see also II, 4. 2).

3. 4. *Rheological Behaviour of Bread Crumb*

When fresh bread comes out of the oven the crust is dry and brittle and the crumb of the bread feels soft and elastic. As bread ages these desirable characteristics are lost, the crust becoming soft and leathery, while a relatively rigid crumb structure is developed. These two changes are the most noticeable to the consumer. The staling of the crust has been shown to be entirely due to absorption of moisture from the interior of the loaf and from the atmosphere. Crumb staling, however, is a far more complex phenomenon. Apart from the crumb's becoming firmer, its swelling power in water decreases rapidly, it dries out by the loss of water and becomes crumbly and less resistant to the action of amylase. Also, the amount of water-soluble starch in the crumb decreases. Finally, X-ray diagrams indicate that in fresh bread the starch exists in both an amorphous and a crystalline form, while in stale bread it exists totally in a crystalline form (KATZ [1928, 1930, 1937]).

The mechanisms of these processes and of bread staling in general, are still not fully understood, although much progress has been made during the past decades. Most investigators believe that staling is due to alterations in the starch (KATZ [1928], SCHOCH & FRENCH [1947]) but there is some divergence of opinion about the role of the two components of starch: amylose and amylopectin. It is also probable that the changes which occur in the gluten to some extent influence staling (ALSBERG [1936]).

From the foregoing it appears that the staling of bread crumb is accompanied by a number of measurable physical changes, which provide bases for several methods of measuring the degree of staling. A review of these methods has recently been made by GEDDES & BICE [1946]. Since the softness of bread appears to be an important criterion to the consumer, the "compressibility" 1) of the bread crumb has most often been measured. As shown by BECHTEL & MEISNER [1952] this method agrees satisfactorily with the consumer's evaluation of staleness and is therefore of real practical value. Nevertheless it should be remembered, as pointed out by CATHCART [1940], that the greatest changes in crumb softness occur within the first ten hours after baking, *i.e.* at a time when most consumers would judge the bread to be fresh.

Bread crumb is not a homogeneous material and it is obvious that the peculiar structure influences to a large extent the behaviour of the crumb when subjected to stress. Moreover size and thickness of the cell walls, as well as moisture content, may vary in different sections of the loaf, thus complicating the measurement of the changes that occur with time. There are two methods for determining the stress-strain relationship, namely measuring the compression produced by a constant load, and determining the load required to produce a given deformation. The former method, used by the majority of investigators, is termed by BICE & GEDDES [1949] the measurement of the crumb softness; the latter method, the measurement of the firmness of the crumb. If, under the conditions of both methods, force were

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1) BICE & GEDDES [1949] point out that the term "compressibility" as used by the cereal chemists, is not in fact applicable to bread compression measurements in which the force is only applied to two faces of the bread section. "Compressibility", as used by the physicists, applies only in cases where the force acts over the whole surface of the test-piece.

proportional to deformation at all test times, it would be possible to make direct comparisons simply by the use of reciprocals. It thus appeared of interest to investigate whether bread crumb obeys Hooke's law, behaving as a perfectly elastic body.

From data from the earlier experiments of PLATT [1930] it would appear that the deformation of fresh bread crumb, when subjected to several different loads, varies directly with the magnitude of the load. BICE & GEDDES [1949] and CROSSLAND & FAVOR [1950] carefully examined the effects of the various fixed conditions on the values obtained in compression tests. By plotting softness against time, the obtained softness curves ordinarily tend to approximate to equilateral hyperbolae. The slope of these curves is constantly changing and depends among other things, on the initial softness and on the time. Thus the initial softness greatly effects the shape of the curves and the conclusions regarding relative staling rates of various breads, drawn from softness curves, may well be erroneous. By using the fixed deformation technique the firmness-time curves are more nearly linear over the customary three- or four-day period of measurement. After the first twelve hours the slope of these curves is fairly constant and appears to be a characteristic of the bread crumb. The loads required to produce a standard compression may therefore be used as a direct indication of differences in the crumb firmness of various breads and as an index of the rate at which the bread crumb becomes rigid.

The relation between deformation and load was found to vary with the age of the bread crumb, becoming more nearly linear up to higher loads as the crumb became less compressible. The relation appeared to be curvilinear for bread only several hours old, even for small loads. Dependent on the choice of the magnitude of force or deformation, the values thus appear to correspond to either the curvilinear, or the approximately linear portion of the curve. Bice and Geddes conclude that under the conditions of their experiments, bread crumb does not strictly obey Hooke's law and that the crumb does not therefore behave as a perfectly elastic body. Both elastic and plastic properties are present. They state that plastic flow is an appreciable factor in the compression when fresh bread is subjected to stress, but that the possibilities for plastic flow decrease when the crumb becomes more rigid. The elastic properties then come fully into play and the behaviour of the crumb closely approaches that of a pure elastic material. In consequence of this the results of the fixed force method (softness curves) cannot be compared with those of the fixed deformation technique (firmness curves) by the simple use of reciprocals.

On the whole the method of fixed deformation has been shown to have definite advantages over the method of fixed force. It is obvious that only a part of the crumb is subjected to stress if a whole slice of bread is used for the compression test. This is undesirable because of the influence of shear at the perimeter of the plunger by means of which the force is applied. To exclude this influence the dimensions of the plunger should equal or exceed those of the test piece. Under such conditions large variations in the thickness of the test piece do not alter the nature of the force-deformation curves.

A different opinion as to the merits of the firmness measurements has been expressed by Bradley who determines the extent of compression of the crumb under a fixed load (BRADLEY [1949], BRADLEY & THOMPSON [1950]).

The measurement of the firming of bread crumb has been widely used to study the effects of certain ingredients on the rate of staling. Since both methods mentioned are used, however, it is not surprising to find that the conclusions of some investigators are at variance with those of others.

4. Rheological Measurements on Cereals

Since the early days of cereal science, numerous attempts have been made to find rheological tests for assessing the quality of a flour. Many of the methods devised are now only of historical interest and but a few have proved to be of practical value for the routine laboratory evaluation of flour. An exhaustive summary will therefore not be given and the description will be mainly confined to those instruments which are widely used today.

Most of the early work was done with dilute aqueous suspensions of flour. The viscosimetric procedure of OSTWALD [1919], LÜERS & OSTWALD [1919a, b, 1920] with the Ostwald viscometer and of SHARP & GORTNER [1923] with the Mac Michael viscometer are well known in this connection. Suspensions of strong flours generally have a high viscosity and the slopes of the linear curves, obtained by plotting logarithmic viscosity against concentration, as well as the viscosities themselves, appear to be related to flour strength. In some cases, especially with soft wheat flours, the viscosity of suspensions, acidulated with lactic acid, can be used to indicate whether the flour is suited for a specific type of pastry product. But on the whole it is not justified to use the data of viscosity measurements alone as a measure of baking quality. The determination of the viscosity of flour suspensions is nowadays replaced by rheological tests on dough.

There have also been devised several instruments by means of which measurements can be made on crude gluten. The expansion of moist crude gluten when heated, the elasticity, the extensibility, the resistance to extension and the force required to puncture a ball of purified gluten, for example, have all been determined. The interpretation of the data from such measurements must be made with care, since it is a question whether the gluten characteristics are fully retained when the gluten has been removed from dough by the conventional washing processes. Moreover, it is highly doubtful whether the rheological behaviour of the gluten alone is sufficiently representative of the condition of the dough since dough properties are also determined by other factors such as starch, flour constituents and water content.

Of the various dough testing instruments now generally used for the commercial evaluation of flour two types may be distinguished:

(a) The recording dough mixers, such as the Hankoczy–Brabender Farinograph and the Swanson–Working Recording Dough Mixer, testing mainly the rate of dough development and behaviour of dough under the stress of extended mechanical action.

(b) Apparatus for measuring the extensibility and the resistance to extension such as the Chopin Extensimeter or Alveograph, the Brabender Extensograph and the Halton Extensometer.

Reference will also be made to the Brabender Amylograph, an instrument for measuring the viscosity of a suspension of flour in water, as the temperature is increased at a uniform rate through the period of starch gelatinization. The amylograph gives useful information about the amylolytic activity of a flour and is frequently used in cereal laboratories. Finally some apparatus will be discussed for determining the rheological properties of bread crumb and of biscuits.

As has been stated before these various instruments, which are mainly empirical in principle, usually measure a complex interaction of several factors. An interpretation of the measurements in terms of definite physical constants is therefore very difficult and often impossible. Nevertheless, these instruments have proved to be valuable tools in the cereal laboratory, since they afford data which have a real meaning in relation to dough behaviour and which can be correlated with various aspects of flour quality.

4. 1. *Farinograph*

The farinograph is a type of slow speed mixer which furnishes information on the mixing properties of a flour. The basis of this instrument consists of a mixing machine, provided with a recording device, originally developed by the Hungarian investigator Hankoczy. Several modifications and refinements of construction were added by Brabender in Germany and the machine was first sold under the name of the Hankoczy–Brabender Farinograph.

> In this instrument the dough is mixed in a water-jacketed mixing bowl, so arranged that water at constant temperature can be circulated through it. Mixing operation can thus take place at a fairly uniform temperature. The blades of the mixing machine rotate towards each other and are geared with a differential of 3 to 2. The force required to turn the two helical spiral mixer blades at constant speed through a dough is measured with a dynamometer. The movements of the dynamometer, as influenced by the varying resistance of the dough to the mixing blades, are indicated by a pointer moving over a scale and are simultaneously recorded by a pen on a moving strip of paper. The graph produced is called a farinogram.

To obtain a flour-water curve a preliminary test is made to determine the water absorption of the flour needed to give a fixed consistency (expressed in farinograph or Brabender units). After adding the main portion of the expected amount of water from the burette to the flour, a few millilitres are added at a time until the curve recorded by the pen runs level for a few moments at the desired consistency. Mixing is stopped, then the mixing bowl and burette are cleaned and the burette is refilled. Mixing is again started with a new portion of flour while on this occasion, the correct amount of water is run in at once. The curve gradually rises until the peak is reached. Depending on the flour, this level is maintained for a while, after which the curve starts to descend. Fig. 4 illustrates the type of farinogram thus obtained. In Fig. 5 farinograms are given of a strong and a weak flour.

It must be remembered that the farinograph curve does not record the true resistance of the dough, since energy is used up in tearing the dough off the mixer blades, as has been shown by DESECK [1939].

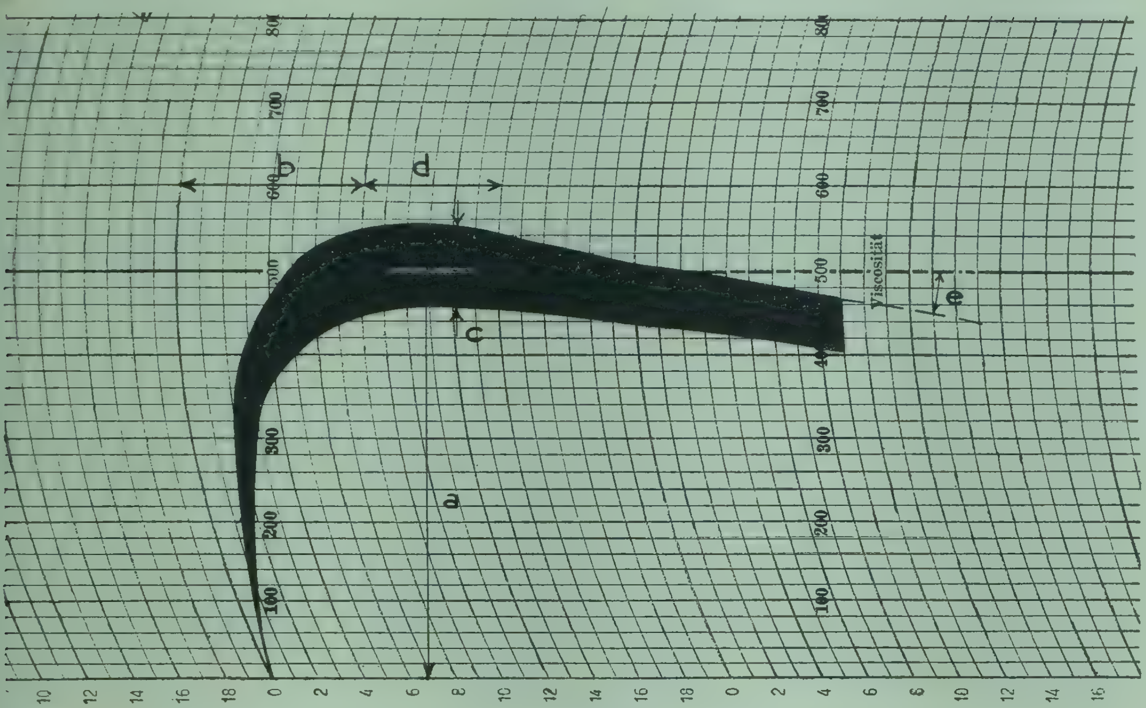

FIG. 4. Schematic farinogram.

According to BRABENDER [1932, 1933] distance *a* represents the consistency of the dough, varying with different amounts of water. Distance *b* is called "the dough development time", which depends on the speed with which water is absorbed by the flour and which indicates a particular dough characteristic. A long development time is usually associated with fairly strong flours. Furthermore, development time is influenced by flour particle size. A coarser granularity generally retards dough development. Distance *d* is a measure of the ability of the flour to withstand mechanical and fermentation abuse and is called "dough stability" or "mixing tolerance". A strong flour maintains a constant consistency for a rather longer period than does a weak flour. The mixing tolerance, as given by the distance *d*, is of special interest to the baker, since it gives an indication of the precision with which mixing operation must be carried out. Thus flour with a low mixing tolerance will be readily overmixed. The angle *e* shows the degree of drop of the curve which is said to be also a measure of stability. The band width *c* was erroneously assumed to indicate the elasticity of the dough. Later, MARKLEY & BAILEY [1938a] showed that band width is a function of the mobility of the dough.

The farinograph may also be used to determine the degree of slack-

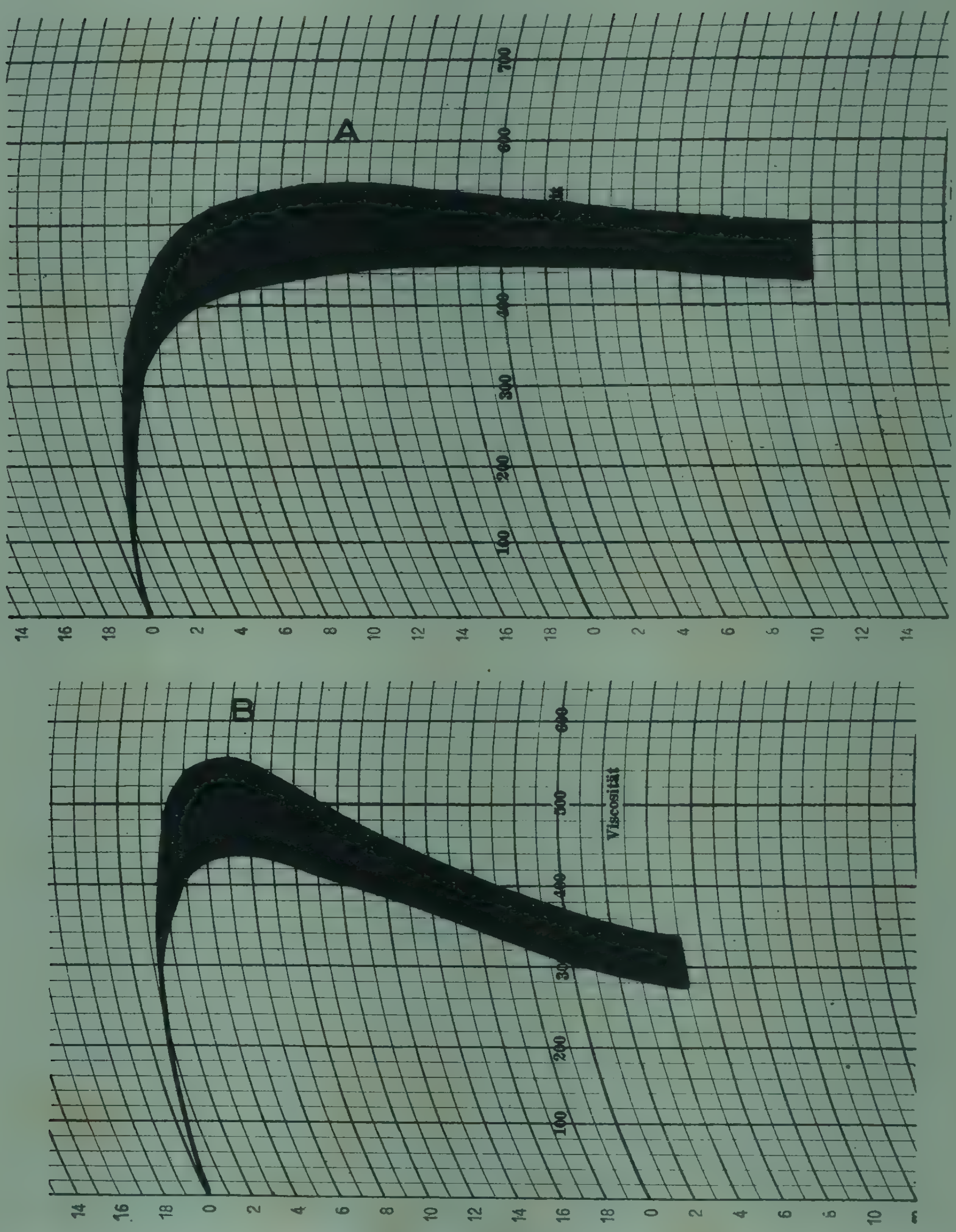

FIG. 5. Schematic farinograms. *Curve A :* strong flour; *Curve B :* weak flour.

ening of the dough during fermentation (BRABENDER [1934]). After adding yeast, salt and the previously determined quantity of water, the dough is mixed until maximum consistency is reached. Mixing is stopped and the dough is allowed to ferment in the mixer for one hour. The paper is moved a little and the dough is now given a two-minute mixing. This is repeated several times for as many hours as the

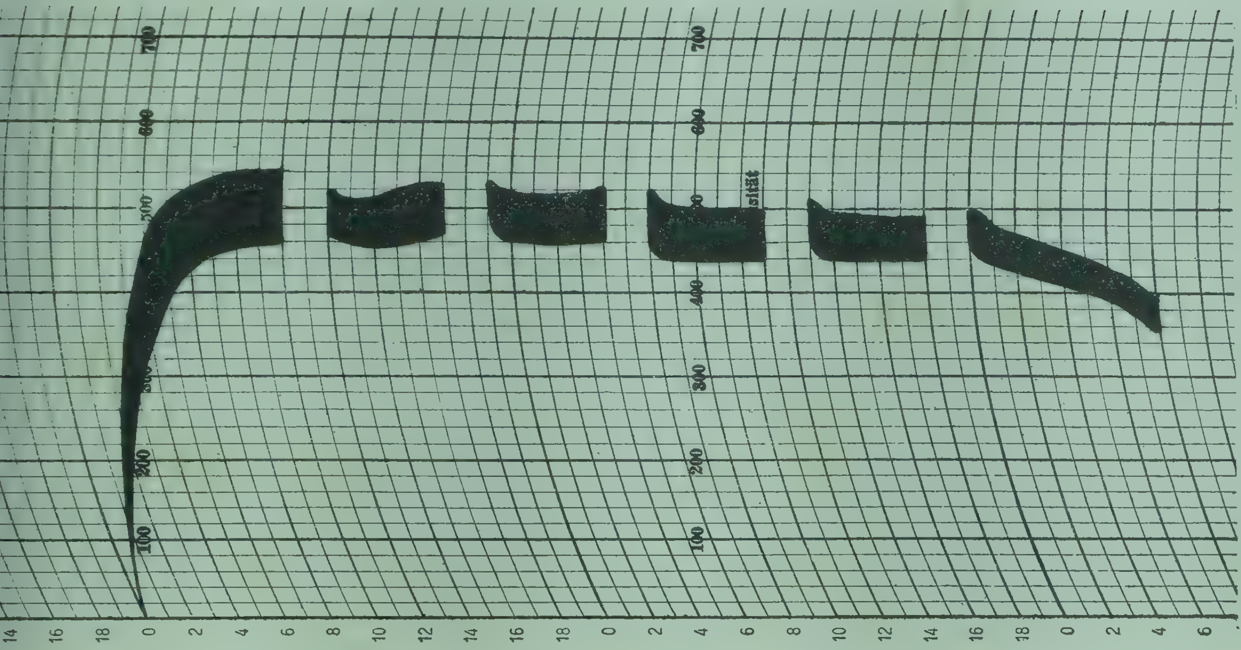

Fig. 6. Schematic fermentation curve.

fermentation is to continue. A typical fermentation curve of a strong flour is given in Fig. 6.

The alterations in dough consistency as produced by the action of enzymes may also be shown with the aid of the farinograph in a somewhat similar manner but without adding yeast to the dough.

The farinograph is one of the most widely used instruments in cereal laboratories and numerous papers have been published dealing with its application to flour and dough problems, the influence of enzymes and dough ingredients on dough mobility and the correlation of farinograph test with baking results.

It should be kept in mind that the mixing bowl is made of bronze and that traces of copper are taken up by the dough during the mixing process. These copper traces act as a catalyst to the processes involved in the action of bromate on flour. As shown by Bungenberg de Jong & Klaar [1939] this copper influences the rheological behaviour of dough.

The farinograph has also been used by Fuller [1938], Freilich [1948] and others to measure the decrease in the consistency of "doughs" of bread crumb and water at constant moisture content, as bread grows stale.

4. 2. *Swanson–Working Dough Mixer (Mixograph)*

Swanson & Working [1933] adapted their mixing machine, originally designed to modify dough by mechanical means (Swanson & Working [1926]) to a recording dough mixer, a high speed pull-fold-repull type of mixer.

> This instrument consists of a vertical cylinder, open at the top, containing four fixed vertical pins at the bottom. A head piece, also containing four pins can be lowered into the cylinder and is rotated by means of a motor. The dough is held back by the fixed pins, while being continuously stretched and folded by the upper pins which have a complex motion. The resistance offered to the movement of the upper pins revolving through the dough is automatically registered on a chart, travelling at a uniform speed. The resulting graphs are known as "mixograms".

The instrument was designed to measure the rate of dough development, the duration of resistance against mechanical action and the rate and extent of increase in dough mobility as a result of mechanical action. A modified form of the recording dough mixer was used by Larmour, Working & Ofelt [1939], which has essentially the same mixing principle but handles only 35 g or less of flour instead of 400 g. This "micro"-form, improved by several modifications, has been used by many cereal chemists.

The value of the recording dough mixer in studying flour properties, the curve characteristics, the influence of several factors on the pattern of the mixogram and the correlation of mixograms with baking results have been fully discussed in a series of papers by Swanson and co-workers (Swanson *et al.* [1936, 1938—1943, 1945], Johnson, Swanson & Bayfield [1943] and Johnson, Shellenberger & Swanson [1946a]).

A typical mixogram is given in Fig. 7. Several lines are drawn which serve to aid in measuring the following characteristics: rate of dough development, time to reach the maximum height, the magnitude of the height of the curve, the rate of weakening and the angle made by the developing and weakening slope.

As soon as mixing starts, resistance is offered to the movement of the upper pins and an almost straight line is drawn by the recording pen as long as considerable amounts of flour have not yet been wetted by water. The point at which the to- and fro-movement of the pen starts, indicates that enough gluten is formed to develop adequate

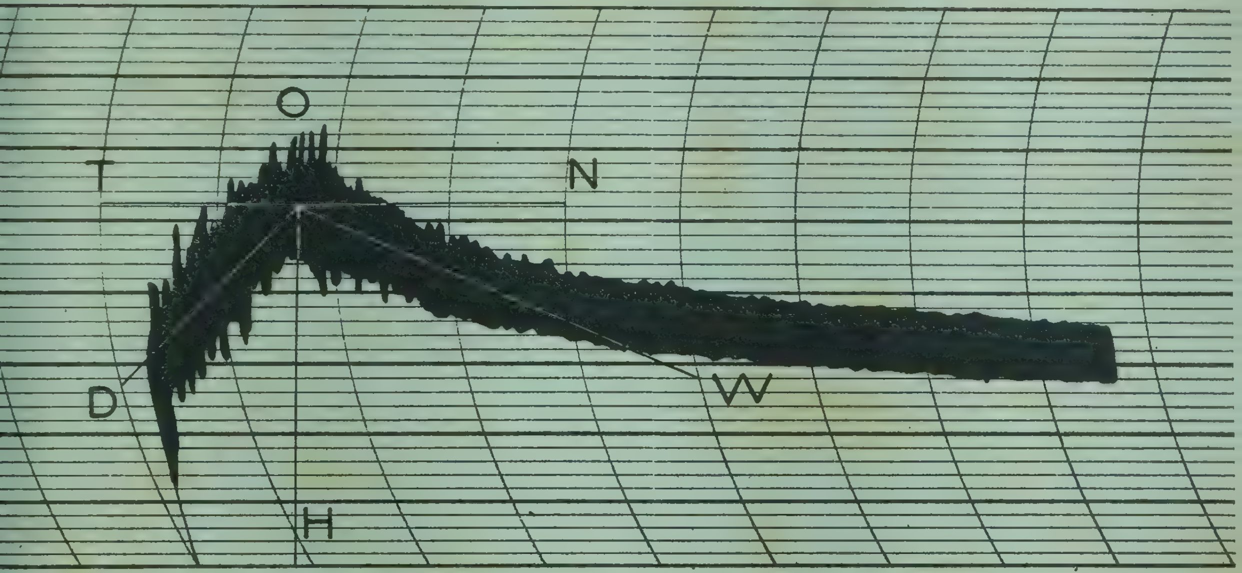

FIG. 7. Curve drawn by the Swanson Working Micro-Recording Dough Mixer.

resistance. At the point O, the dough has reached minimum mobility. The line T O indicates the time needed to reach this minimum dough mobility, whereas the angle D O T indicates the rate of development. The height of the mixogram, as given by H O, is determined primarily by the protein content and secondarily by the water absorption of the flour. From the point O dough mobility increases. The rate of dough weakening is measured by the angle W O N. According to Swanson the range of mixing tolerance is measured by the angle D O W its magnitude depending on the rate of development and the rate of breakdown of the dough. The slower these rates, the larger the angle D O W, the wider range in tolerance to mixing. With different types of flour the slope of the weakening line W O will vary considerably, from nearly horizontal to very steep; whereas in some cases the last part of the mixogram will be concave, in other cases nearly straight. The first part of the weakening slope is the most significant and hence the line W O is drawn in its centre. Fig. 8 illustrates the type of mixograms characteristic of a high and a low protein flour.

Other mixogram characteristics may be used in addition to those already mentioned, namely the width of the mixogram at the peak and at the last part of the weakening slope and the area under the mixogram from the starting point to the point of minimum mobility. The latter is an indication of energy input required to mix a dough to

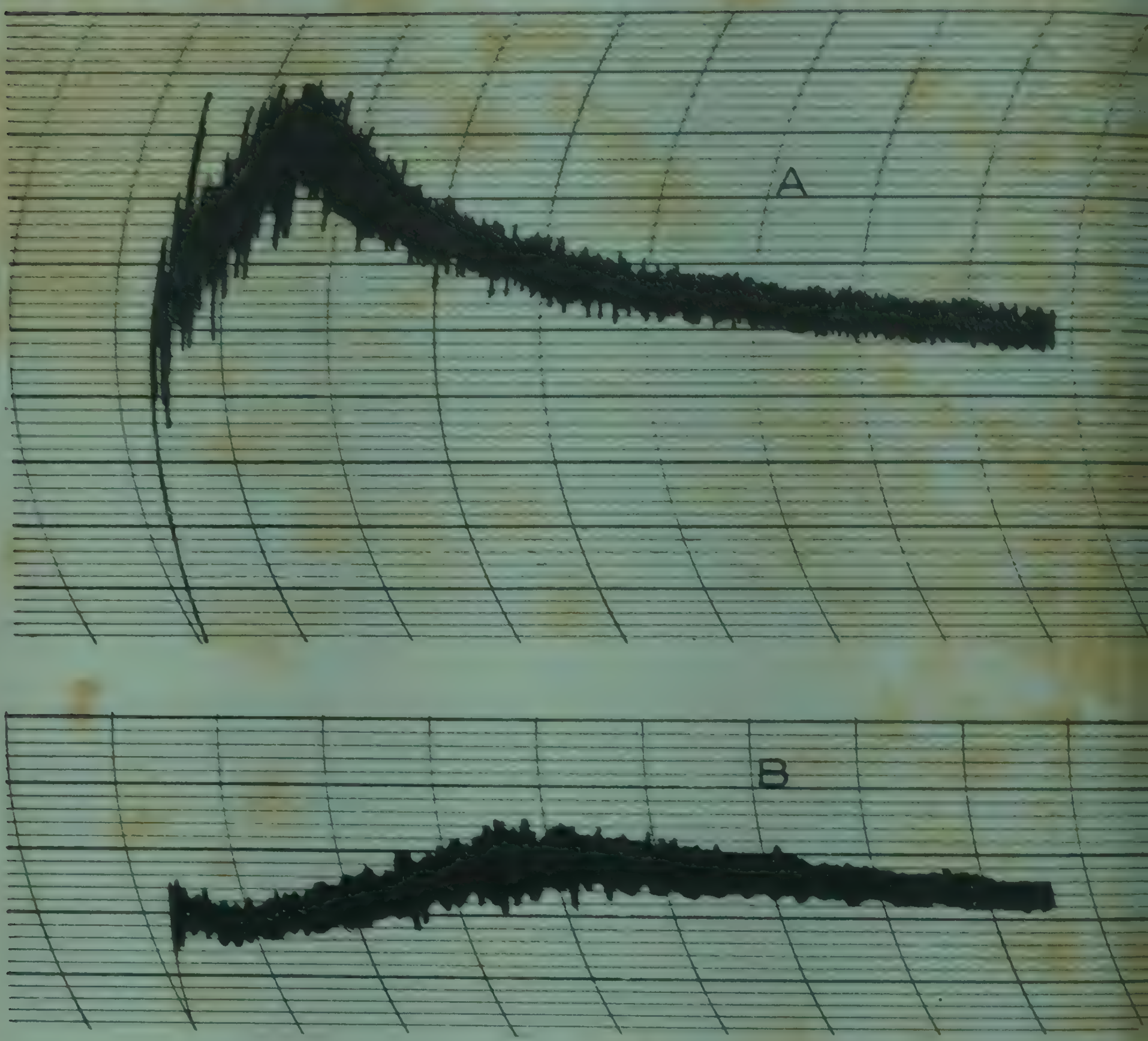

FIG. 8. Mixograms. *Curve A*: mixogram of high protein flour; *Curve B*: mixogram of low protein flour.

optimum development. HARRIS, SIBBITT & BANASIK [1943] evolved a single figure score indicative of loaf volume from several mixogram characteristics. The authors made mixograms from doughs containing the usual baking ingredients and these were mixed and fermented for three hours in the same manner as for baking bread. Under these conditions a high correlation was found between calculated and actual loaf volume.

On the whole, the most important use of the dough mixer appears

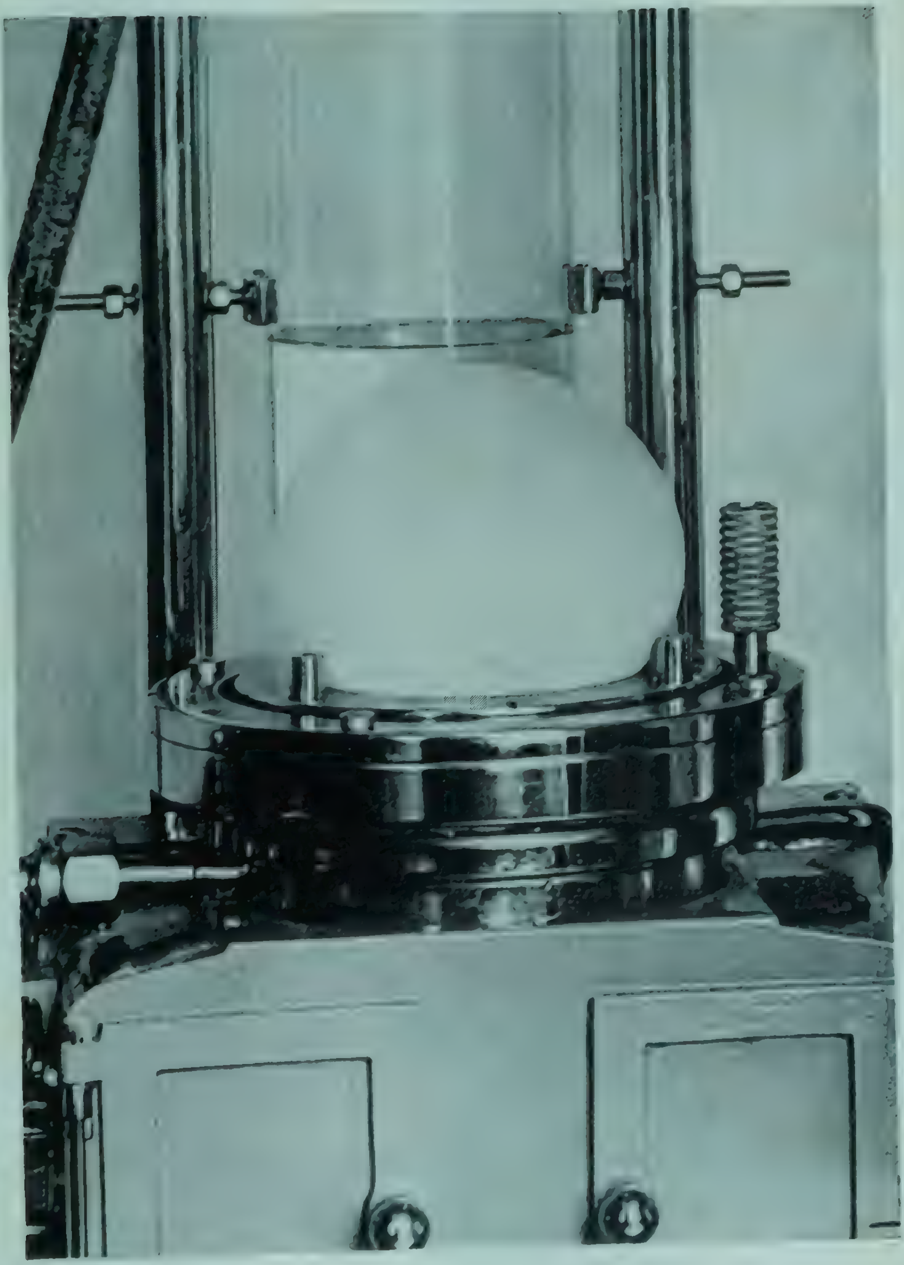

FIG. 9. Dough bubble produced by the alveograph.

to be that of furnishing information supplementary to baking data, such as mixing requirements and mixing tolerance. Since protein content to a large extent determines the mixogram pattern and since protein content is to a considerable extent responsible for flour strength, mixogram characteristics may serve to aid in flour classification when fine distinctions between groups and types are not required. In particular the instrument has been proved to be useful in determining the varietal pattern of flours.

In comparison with the farinograph the treatment of the dough is much more severe. The action of the mixograph is more a stretching and less a kneading, while that of the farinograph is more a kneading and less a stretching. As a consequence of this the dough usually develops more slowly with the farinograph.

4. 3. *Chopin Extensimeter or Alveograph*

This instrument is designed to measure extensibility and resistance to extension of a thin sheet of dough (Chopin [1921]). The idea underlying the principle of the extensimeter was to imitate as nearly as possible the processes which the dough undergoes in actual bread making, i.e. a transformation of the dough from a compact state into thin membranes. The ability of the dough membrane to stand being extended during rising and baking is of importance for the ultimate bread volume and the structure of the bread crumb.

> The pressure on the dough sheet is exerted by means of a carefully controlled flow of air by which the sheet is extended into a bubble (Fig. 9). Pressure is continued until the dough bubble is ruptured. The changes in air pressure during the test are automatically recorded on a curve. The test doughs are all made up to contain the same quantity of water and are prepared under strictly defined conditions. After a rest period at a constant temperature, the dough sheet is placed between two metal plates, the upper one having a circular hole through which the dough sheet is blown into a bubble by air pressure admitted through a small valve in the lower plate. The valve is connected with a large graduated burette by way of a small air chamber. By allowing water from a bottle to flow into the burette, air is displaced and this provides the pressure.

The instrument is rather complicated and some manipulative skill is required of the operator; moreover, careful attention must be given to the preparation and the handling of the dough sheet.

Fig. 10 illustrates the type of curve traced by the alveograph. The resistance of the dough to expansion is greatest at first and the pressure reaches its maximum P very quickly. After this maximum, there is a marked decrease in pressure, fairly rapid in the beginning but becoming more gradual later until the point (M) is reached where the dough bubble ruptures. The total deformation is divisible into elastic and plastic deformations. After rupturing the walls recover to about one-half their extended area, which means that about half the strain is non-recoverable because of stretching beyond the elastic limits. The height PQ indicates the tensile strength or stability of the dough in its initial state, whereas the height MN is a measure of the strength of the dough at the time of rupture. The extensibility is shown by the line ON. The total volume of the dough bubble may be read on the graduated burette or may be determined by measuring the total area under the curve by means of a planimeter.

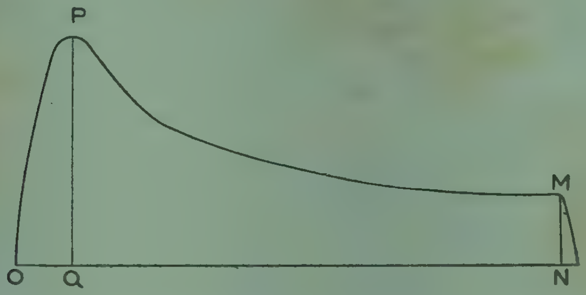

FIG. 10. Schematic diagram of the curve traced by the Chopin Alveograph.

The maximum pressure P, the square root of the volume before the bubble bursts G and a figure W, which is a function of the area under the curve, were used by Chopin to characterize the flour. W is a measure of the work done in blowing the bubble and appears to give a good indication of the general strength of the flour.

The shape of the curve varies with the characteristics of the flour. In general a dough made from a strong flour will stretch further before rupturing of the bubble, than a dough made from a weak flour.

According to SCOTT BLAIR & POTEL [1937] the alveograph indicates primarily the water absorption capacity of the flour and measures a complex function of viscosity and modulus. P appears to be directly related to viscosity and G to depend on the product of a function known to be related to spring and one related to shortness. A high viscosity and a low modulus are the most important factors involved in producing a high value of G.

4. 4. *Brabender Extensograph*

The Brabender Extensograph, first described by KUHLMANN [1936], also measures the extensibility of a dough and the resistance to extension by applying a force to a strand of dough until it ruptures. The instrument has the advantage that fermented doughs may also be tested, and it adequately registers the effect of oxidizing- and reducing substances upon the properties of flour doughs.

The dough to be tested is preferably prepared in the farinograph under defined conditions. A definite quantity is rounded and moulded mechanically into the form of a solid cylinder, which, supported by a special cradle to which it is held by clips, is engaged and stretched by an arm moving vertically on a guide and driven by a motor. As the dough is extended, force is exerted, which is transferred through a system of levers to a stylus, recording the force on an automatically operated chart.

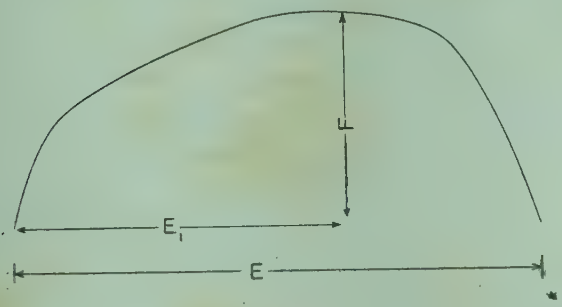

FIG. 11. Typical Extensogram.

A typical "extensogram" is shown in Fig. 11. The following constants are usually taken from the extensogram:

F = force applied to extend the dough at constant speed of extension.
E = extensibility.
E_1 = extension to optimum point of resistance to extension.
A = area under the extensogram.

The initial sharp rise in the curve is explained by FISHER, AITKEN & ANDERSON [1949] by assuming that because of the cohesive forces within the resting dough, no appreciable stretching can take place before a certain stress is imposed. The gluten network is then extended and the elastic properties of the dough start to offer resistance to the continuous stretching. This resistance lessens as the elastic limit is progressively exceeded at various points, until at the highest point of the curve all elasticity has been overcome. During this process, represented by a continuous rise in the curve, plastic deformation also takes place. The remaining part of the curve after the peak is proposed to represent continued plastic deformation. The elastic properties of the dough are hence probably much more reflected by the quantity E_1, than by E.

The ratio of F to E is significant in characterizing a flour in relation to breadmaking quality, whereas A appears to give an indication of flour strength. A certain balance between extensibility and resistance to extension is required in order to obtain optimum baking results, whereas a certain height of the curve is also desirable.

Extensograph studies made by MUNZ & BRABENDER [1940a, b, 1941], AITKEN *et al.* [1944], MERRITT & BAILEY [1945] and JOHNSON *et al.* [1946b] have shown that a positive relationship exists between extensogram dimensions and protein content of the flour and that extensogram data are of value in assessing baking quality and in classifying flours for specific uses. Oxidizing agents such as potassium bromate effect a decrease in extensibility and an increase in resistance to extension. Reducing agents effect the reverse. These effects are not only related to the type and amount of the added substances but also to the time in which they act and the physical manipulation of the dough (SMITH & ANDREWS [1952]). Recently DEMPSTER, HLYNKA & WINKLER [1952] used a modified technique for analyzing extensograms in an interesting study of the bromate reaction and the behaviour of dough.

4. 5. *Halton Extensometer*

Based on the fundamental studies on the rheological behaviour of dough carried out by Halton and co-workers, Halton devised the extensometer, which apparatus has already been dealt with in section 2.

In comparison with similar instruments already discussed, the Halton Extensometer has some characteristics in common with the Brabender Extensograph. However, the extensometer has a specific feature in using a dough which has been adjusted to a certain modulus at the time of stretch. Consequently the curve obtained may be interpreted rather conveniently in terms of well-defined rheological properties. In this respect the Halton instrument has a definite advantage over other instruments of similar type. So far no extended reference has been made in the literature concerning the results of extensometer tests. According to HALTON [1949a] and HALTON & GREER [1950] the instrument not only proved useful in the examination of flours for bread-making purposes, but also in assessing the biscuit-making [1] quality of weak wheat flours. In the latter case the desired characteristics appeared to be low elasticity and high extensibility.

4. 6. *Brabender Amylograph*

The amylograph is a torsion viscosimeter originally designed for the investigation of rye flour (BRABENDER [1937]). This instrument records automatically the changes in viscosity of a flour-water suspension as the temperature is uniformly increased. Since the principle of the amylograph and the interpretation of the curves obtained (amylograms) have been discussed in chapter I, it will suffice to mention only the use made of the amylograph in the cereal laboratory.

The viscosity of a flour suspension increases as the starch gelatinizes but this increase is opposed by the liquefying action of the amylases present. The height of the amylograph curve is therefore largely dependent upon the alpha-amylase content, a high curve indicating little alpha-amylase activity and a low curve excessive amylase activity. The latter is of special interest in the case of sprouted grain which has an undesirable effect on the bread crumb, because of the marked liquefying action of alpha-amylase. Several other factors, however, influence paste viscosity: such as starch and protein content, pH and the extent of mechanical injury of the starch granules, suffered during the milling process. These factors interfere with the interpretation of the amylogram and the maximum paste viscosity alone cannot therefore be used as a direct index of alpha-amylase activity. The amylograph is particularly useful for the testing of rye flours, whose baking value is mainly governed by a proper balance between starch gelatinization and amylolytic activity.

SELMAN & SUMNER [1947] proposed an amylographic procedure for controlling the diastatic supplementation in baking. This procedure, however, does not work with the recently developed fungal amylase preparations because of their rather low thermostability, as a consequence of which the enzyme is inactivated before the temperature of starch gelatinization is reached. MARNETT *et al.* [1948] describe a modified amylographic technique for a rapid evaluation of amylase activity, whereas BROWN & HARREL [1944] and BRABENDER, MÜLLER &

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1) (See Introduction).

Köster [1937] employed the amylograph to classify rye flours on the basis of their baking value.

4. 7. *Apparatus for Determination of "Compressibility" of Bread Crumb and Breaking Strength of "Cookies"* [1]

Several methods for determining the "compressibility" of bread crumb have been described by Katz [1928], Platt [1930], Bailey [1930], Nikolayev [1941], Combs [1944], Straub & Hirsch [1935], Hintzer [1949] and Cornford & Coppock [1950]. All of these instruments operate on the same principles. The bread crumb is subjected to a fixed weight for a given time and the total deformation is measured (measurement of crumb softness), or the weight needed to produce a fixed depression is determined (measurement of crumb firmness). As has been discussed in II, 3, the last method has proved to be the most satisfactory. By allowing the bread crumb to spring back towards its normal shape after a certain time of application of load, the percentage of rebound may also be calculated. This has been shown to be of particular value in the case of gummy or sticky bread crumb, which shows a low percentage of rebound, contrary to the crumb of a high-quality bread, which recovers a fairly large percentage of its original form.

Platt & Powers [1940] describe an apparatus, designed by Baker, in which a flat disc is pressed against the surface of the crumb. Force is progressively applied by means of a lever and winch operated by a motor. Force and deformation values can be read from scales at any moment during the test. According to Bice & Geddes [1949] crumb firmness can be measured with this instrument with more precision than crumb softness.

Favor & Johnston [1947], using the fixed deformation technique, found that the synthetic surface-active agent poly-oxy-ethylene stearate (p.o.e.s.) progressively reduced the rate of development of firmness of the crumb as the quantity of the surface-active agent was increased. Edelmann & Cathcart [1949] using the same principle, investigated the effect of 24 different surface-active agents. None of these compounds appeared to be as effective as p.o.e.s. although glyceryl monostearate and glyceryl oleostearate also lowered the rate of increase in crumb firmness upon storage significantly. These results were confirmed by other workers (EDELMANN, CATHCART & BERQUIST [1950], SKOVHOLT & DOWDLE [1950]).

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[1] (See Introduction).

Fats, glycerides and lecithin appear to have the same effect, though less marked. It is assumed that by the action of these adjuncts a finer cell structure is obtained resulting in an increased tenderness of the crumb. The actual mechanism, however, is very complex and the theories which have been advanced (PLATT & FLEMING [1923], BAKER & MIZE [1942]) cannot explain all the facts.

Various sugars, dextrines, malt extract and, in recent years, fungal enzymes have also been found to retard the rate of crumb firming.

It has often been claimed that these ingredients which reduce the rate of firming of the bread crumb also retard staling. It should be remembered, however, that the firming of the crumb is only one aspect of the staling process and that the interpretation of the results of firmness measurements must be made with care. Actually, it is highly improbable that these adjuncts affect the real staling mechanism.

Procedures for measuring the resistance of the crumb and crust of bread to shear are given by COMBS [1944] and WOLODKEWITSCH [1950] but few such measurements have been made as far as the authors are aware.

The breaking strength of "cookies" and other baked products is usually measured by exerting a force across the centre of the test-piece, which is supported by two parallel rails. At the instant when the test piece breaks, the maximum force is noted. Two devices for measuring the breaking strength have been described by DAVIS [1921] and a similar instrument "the automatic shortometer" was designed by BAILEY [1934]. Experiments have shown that a considerable number of replicate measurements is required and the instruments must therefore permit of rapid operation.

CHAPTER III

RHEOLOGY OF MILK, CREAM, ICE-CREAM MIXES AND SIMILAR PRODUCTS

BY

G. W. SCOTT BLAIR

NATIONAL INSTITUTE FOR RESEARCH IN DAIRYING, THE UNIVERSITY OF READING, ENGLAND

0. Introduction

Measurements of the viscosity of milk were made before the end of the last century, mainly with a view to finding a property which might prove useful as an index of quality, thus avoiding lengthy analyses. This hope was never fulfilled. Moreover one famous set of data, quoted many times since, has recently been shown to have been faulty.

Milk deviates but little from Newtonian behaviour, though its viscosity is not easily measured accurately because of creaming. Cream shows a variety of rheological anomalies and it is difficult to define any suitable set of properties by which to describe what the consumer means by "body". The flow properties of condensed milk are important during manufacture but are commonly assessed subjectively. The rheology of cream is often considered in relation to that of butter prepared from it and the latter is dealt with in Chap. IV.

1. Milk

These facts make for considerable difficulties in arranging a neat classification of materials and methods in the present chapter: many of the researches overlap both with respect to materials studied and methods used.

Data on ice-cream mixes are scanty. No doubt many experiments have been done but few are published. Some of those researches which are described in the literature include ice-cream mixes together with creams, mayonnaise and other materials.

It has therefore seemed best, while attempting a rough classification by materials, to follow the subject matter as far as possible, chronologically. But both systems can only be somewhat loosely followed. Work on rennetted milk is dealt with in Chapter V.

Cox [1952] [1]) has recently published an interesting paper containing a useful survey of the principal researches on viscosity of milk and the author gladly acknowledges the use here made of Cox's article.

SOXHLET [1876] determined the outflow times, in a Reischauer capillary viscometer of both water and milk at a series of temperatures. Unfortunately he appears to have failed correctly to interpret a serious error in his relative viscosity at the all-important temperature of 20° C, i.e., the temperature at which the viscosity of water happens to be almost exactly 1 cp. As Cox points out, this incorrect figure has been quoted and re-quoted without criticism in subsequent work.

WOLL [1895] studied the effect of heating milk on its viscosity. An early study of milk viscosity was also made by BOGDAN [1905].

KOBLER [1908] made a careful and systematic study of the variation of viscosity of milk with temperature. Between 15° and 25° results were claimed to have an accuracy of about 2 %: at lower temperatures, errors were $\sim 5 - 10$ %. At 25° C the viscosities of eight typical samples, relative to water, varied from 1. 7 to 2. 0 approx.

TAYLOR [1913], starting with milk cooled to 20° C, showed that, on raising the temperature progressively, the viscosity passed through a minimum at 60 — 65° C, and that at 75 — 80°, the viscosity was higher than that of the raw milk. A not very happy attempt was made to express the results in terms of an empirical equation.

EVENSON & FERRIS [1924] also studied the effects of pre-heating milk and obtained a curve similar in form to that of Taylor. They proposed the application of the Einstein formula.

WHITAKER, SHERMAN & SHARP [1927] studied the effects of half-an-hour's heating to various temperatures on the viscosity of skim milk and whey, measured at 24° C. For the former material, the viscosity rises progressively: for the latter a maximum is passed corresponding to a temperature of 100° C.

BATEMAN & SHARP [1928a], showed that the viscosity of milk, whether whole, condensed, pasteurized or skimmed, falls with rising stress. Repeated shearing reduces viscosity, but part of the loss is re-gained on standing, except in the cases of skimmed and homogenized milk. The viscosity of skim milk increases with age. Homogenization causes an increase in viscosity: pasteurization, a slight fall.

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[1]) I am indebted to Mr. Cox for a number of helpful suggestions in the writing of this chapter. G.W.S.B.

Viscosity is not a simple function of solid matter content. RAHN & SHARP [1928] give an excellent summary of work to date.

MOHR & OLDENBURG [1929a, b] apply the Ostwald–de Waele equation to data for milk and cream, obtained both with Couette and Ostwald type viscometers, and also with a falling cylinder viscometer. (vide OSTWALD [1925a, b, c, 1927], DE WAELE [1926]). The results with the three types of viscometer agree none too well. Hatschek's concentration equation does not hold for concentrations of fat > 3 %, taking the "viscosity" from the straight portion ("Laminarast") of the flow-curve. The effects of souring, heating and cooling are discussed: for capillary viscometers alone, the 4th power radius law is well followed. MOHR & BROCKMANN [1930] measured the surface tensions of milks and also surface viscosities and rigidities which would seem to depend largely on the amount and nature of the fat.

LEIGHTON & LEVITON [1932] claimed that the addition of sugar to skim milk first diminished and only on further additions, increased the viscosity (see also III, 4).

TAPERNOUX & VUILLAUME [1934] published a very careful study, using a modified Ostwald viscometer, of the viscosity of a single milk, before and after removing the fat, at nine temperatures ranging from 0 — 40° C. A hyperbolic relation is suggested. Viscosities of 14 individual milks and of a mixture of all of them, were determined at a single temperature and compared with titratable acidity, density and fat contents.

RIPAU–TILICI & DRĂGULESCU [1936] discuss densities and viscosities of milk in relation to detection of adulteration but do not propose any very precise procedures.

SPÖTTEL & GNEIST [1942] using a Höppler "rolling sphere" viscometer, compare the viscosities of milk from the cow, goat and ewe at temperatures from 10 — 50° C. Although the number of samples is not clearly stated (it would appear to be ~ 20) the following correlation coefficients with viscosity are of interest:

(1) *Dry matter*	(2) *Fat free dry matter*	(3) *Protein*	(4) *Fat*	(5) *Protein and Fat*
.65 ± .12	.66 ± .08	.42 ± .17	.24 ± .18	.43 ± .16

(1) and (2) are claimed as significant; (3) and (5) as showing a strong correlation tendency and (4) as doubtful.

The increase in viscosity of cow's evening milk compared with morning milk is greater than would correspond to the increased fat content. Differing from capillary viscometry, the Höppler viscometer does not lower viscosity appreciably as a result of repeated shearing.

During the second world war, a number of rheologists in the Netherlands, unable to continue their normal activities, did experiments on dairy products. EILERS & KORFF [1945] measured the voluminosity of milk and also studied electroviscous effects. They showed that milk has its minimum viscosity at its natural pH. Skim milk is a polydispersed system for which the usual voluminosity equations are hardly applicable. Pasteurization increases the voluminosity. This and later work is fully described in a monograph by EILERS, SAAL & v. D. WAARDEN [1947].

SEIDLER & ELKE [1949] find but small effects of season, period of lactation and even fat content on viscosity-temperature changes as measured with a Höppler viscometer.

CAFFYN [1951] made careful measurements, using a capillary viscometer, on six samples of homogenized milk at temperatures from 20° — 80° C. The accuracy was estimated at 1 %. Changes in viscosity due to previous heating of milk were found but were not great enough to justify hopes of a test for correct pasteurization. The changes observed are ascribed to changes in protein since they occur in supercentrifuged samples; but the fall in viscosity produced by shearing depends on changes in the fat. Curves plotting log η against 1/T tend to show a break at about 40° C. Caffyn suggests that the fat particles did not melt until a temperature a few degrees above their normal melting point had been reached.

COX [*loc. cit.* 1952] discusses the functional relation between viscosity and temperature and sees no particular *a priori* reason to rely on the Guzmán–Andrade type of equation. He uses an empirical equation of the form

$$\eta_\theta - \eta_{20} = b_1 (\theta - 20) + b_2 (\theta - 20)^2 + b_3 (\theta - 20)^3$$

when η_θ is absolute viscosity at θ° C
η_{20} is absolute viscosity at 20° C

and b_1, b_2, b_3 are disposable parameters which he calculates for the data of Tapernoux and Vuillaume, Spöttel and Gneist, and Caffyn (*loc. cit.*). For relative viscosities $b_3 = 0$ and the other parameters have been calculated for the data of Soxhlet, Kobler and Taylor.

In his summary Cox concludes: "It has been suggested that values for the relative viscosity and viscosity of whole milk cannot usefully be regarded as independent of the experimental circumstances in which the observations were obtained."

In relation to flow in pasteurizers, admitted to be turbulent, SELL [1941] has shown how flow might take place were it streamline, but his purpose is not clear to the author.

BELL, CURRAN & EVANS [1944] have studied the effects of time and temperature of sterilizing on the rheological and other properties of evaporated milk. High temperatures and short times favour good colour and flavour but lower temperatures and longer times are superior rheologically. DEYSHER, WEBB & HOLM [1944] have also measured the viscosities of evaporated milks. WEBB & HUFNAGEL [1948] study the effects of different types of agitating and of temperature and time differences on the viscosity of concentrated skim milk.

TORSSELL, SANDBERG & THURESON [1949], using a Höppler viscometer, have followed the changes in viscosity of 3 % fat standardized milk during drying. The percentage of total solids is given by the expression

$$\frac{a \log (T/b) - \log \cdot \log \cdot (\nu + 0.8) - c}{d \log (T/b) - f}$$

(where T is temperature (°K) and ν is kinematic viscosity). (This expression is derived from the Walther formula).

STEBNITZ & SOMMER [1935a, b], using an electrically recording falling sphere viscometer, have studied seasonal variations in consistency of sweetened condensed milk, which thickens on ageing (MacMichael and capillary viscometers had been tried and discarded). The effects of fore-warming conditions are also discussed.

REINER, SCOTT BLAIR & HAWLEY [1949] showed that some aged sweetened condensed milks are not only thixotropic but also show a Weissenberg effect, climbing a rod rotated vertically in the milk. It is suggested that the effect may be due to denaturing of proteins.

2. Consistency of Cream

Ever since Aristotle wrote of " *τὸ παχύτεϱον τῶν γαλαϰτων*", it has been impossible to draw a clear distinction between work on milk and on the cream which is separated from it either by standing under the influence of gravity or, in modern times, by the centrifuge.

As far back as 1896, Babcock & Russell [1896a, b] studied the effects of pasteurization on the consistency, not only of milk but of cream; and Dumaresq [1913] later investigated the flow of cream in an Ostweld viscometer, studying the effects of previous heating. He found a power-law relation between viscosity and fat content.

But the first comprehensive investigation was that of Palmer & Anderson [1926], who found, for raw milk of uniform fat content, that the volume of cream rising is closely related to the solid-not-fat content and that the viscosity is highly correlated with both. For pasteurized milk, however, it is claimed that viscosity is only a minor factor in relation to creaming. These findings have a close bearing on the loss of cream-line associated with pasteurization, especially when this is excessive.

In the same year, Sherwood & Smallfield [1926] studied the effects of pasteurization on both cream and ice cream mixes, using a Scott (orifice) and a Doolittle (torsion) viscometer. Pasteurization tends to diminish viscosity but the less obvious conclusions would seem to be somewhat confused. Two years later, Pyne & Lyons [1928] showed that the viscosity of cream from pasteurized milk could be increased by chilling before separating, or by the addition of lactic acid.

Babcock [1931] made a microscopic examination of the clustering of fat globules in cream, comparing his observations with data from a Saybolt viscometer. In fresh cream, the fat globules remain single, the subsequent rate of clumping being greatest at temperatures $\sim$ 7—8° C. Hardly any clumping occurs at 60° C. The effect of pasteurization in reducing viscosity is only marked at higher "acidities".

Nair & Mook [1933] measured times of outflow of creams through a short capillary (diam. $\sim$ 2 mm) attached to a milk bottle — the so-called "Borden Body Flow Meter". The effects of ageing, temperature, etc., and such phenomena as thixotropy are discussed. Three years later, Henderson [1936], using the same type of apparatus, showed that the viscosity could be raised by suitable agitation of either the milk or the cream. The viscosity of pasteurized cream is slightly higher when aged as cream, than when aged as milk. The effects of cooling treatments on viscosity are much less in cream made from pasteurized milk than in that from raw milk.

Leviton & Leighton [1936] claim that Taylor's equation holds for unclumped cream and that discrepancies from this equation give some indication of the degree of clumping. (TAYLOR [1932])

$$\frac{\eta_{\text{cream}}}{\eta_{\text{serum}}} = \frac{1 + 2.5\,\eta_{\text{fat}} + {}^{2}/_{5}\,\eta_{\text{serum}}}{\eta_{\text{fat}} + \eta_{\text{serum}}} \cdot \phi$$

where ϕ is volume concentration. Viscosities were measured at 64° C.

SCOTT BLAIR, HENING & WAGSTAFF [1939] studied the flow of true cream, homogenized cream, and of cream reconstituted from butter fat and skim milk, in a double-bulb capillary viscometer in which the driving pressure could be held at a variety of controlled values. At 37° C, almost every conceivable type of flow anomaly was found but, although in general natural creams showed simpler flow behaviour than did reconstituted creams, no very definite test for the latter was established. A breakdown of structure was observed through the flow curves, however, long before it could be detected under the microscope.

WIESE, NAIR & FLEMING [1939] ask which of the constituents of milk is responsible for the phenomena of "rebodying", (an ugly word used to describe improvements in consistency of cream induced by heating and cooling processes). They conclude that the membranes surrounding the fat globules are mainly responsible but that there are also compounds in the aqueous phase which help.

SKELTON & SOMMER [1939—40] have studied "rebodying" using a Gardner Mobilometer (a sinker viscometer), capillary viscometers being rejected on account of the danger of blocking of the capillaries. They mistrust conclusions drawn from a microscopic examination of diluted cream since the clusters of fat particles are broken up on dilution. SKELTON & HERREID [1941] using the Borden Body Flow Meter, conclude that for unpasteurized cream, rebodying treatments are more effective in winter than in summer: pasteurized cream shows little seasonal difference. HENING & DAHLBERG [1943] study the effects of varying times and temperatures of pasteurization using a MacMichael viscometer. BELL & SANDERS [1946] also use a MacMichael viscometer, and conclude that the use of fresh milk, containing unclumped fat globules, quick freezing and low storage temperature, produces a stable emulsion of good body when thawed after several months' storage.

Good "body" in cream is important mainly because the consumer tends, often erroneously, to judge "richness" in terms of body, much of which is often "false". The maintaining of the "false body" in cream is more difficult in countries where household supplies are not normally stored in refrigerators. But body is also important in relation to butter-making, a subject discussed in the next chapter. Thus VALENTINE & SARGENT [1935] have studied the relationship between rates of cooling of cream and the spreadibility of butter made from it, and MOHR & WELLM [1948], measuring the viscosity of cream in a Höppler consistometer, relate viscosities to conditions of packing of the fat globules, which they regard as an important factor in the Fritz process of continuous butter-making.

3. Body of Ice-cream Mixes

(Note: For a general account of work in this field, the reader is referred to "The Ice Cream Industry" by TURNBOW, TRACEY & RAFFETTO [1947]).

In an early attempt to differentiate specifically between Newtonian and Bingham-plastic behaviour, MASUROVSKY [1925] showed that, with a MacMichael viscometer, whereas milk and cream (20 % and 40 %) showed almost perfectly Newtonian behaviour, ice cream mix gave a linear flow-curve which, on extrapolation, made an intercept on the stress axis.

BATEMAN & SHARP [1928b] also found a linear relation between shear stress and rate of flow for ice-cream mixes. Leighton and his colleagues made a fairly complete study of the rheology of these systems. (LEIGHTON & WILLIAMS [1927a, b], KURTZ [1929], LEIGHTON & KURTZ [1929], LEIGHTON & WILLIAMS [1929]). Their conclusions may be summarized as follows:

The viscosity of ice cream mixes rises on ageing and falls on stirring. The "basic" (stirred) viscosity is related to concentration by the Arrhenius logarithmic law. Measuring the time taken to fill a capillary under a series of suction pressures, the stress/shear-rate curves are found to be linear. In a later paper, LEIGHTON, LEVITON & WILLIAMS [1934] calculate the viscosity of mixes from the sagging of a cylindrical "beam" specimen, using Trouton's equation: (TROUTON [1906])

$$\eta = \frac{5\,gml^3}{1152\,v\,(0.049\,d^2)}$$

where η = viscosity
m = mass
l = length
d = diameter
v = rate of sag
$0.049d^2$ = moment of inertia.

The viscosity is related to fat and gelatine contents but the correlation with general quality is not complete.

Whitaker and his colleagues (Whitaker [1929], Whitaker & Herrington [1929], Whitaker & Hilker [1938]) use a torsion pendulum viscometer for ice cream mixes as well as for milk and cream and have invented a mechanical device for breaking down mixes to give a reproducible basic viscosity. They have also studied the effects produced by superheating condensed skim milk for addition to ice cream mixes and conclude these effects are not primarily a matter of viscosity changes. Hening [1931] concludes that "basic viscosity" is not to be regarded as the minimum possible value of viscosity following a complete mechanical breakdown, but rather as an arbitrary but useful concept when a standardized method of agitation has been used.

Penczek & Dahlberg [1940] describe a hand emulsifier as a convenient means of breaking down false-body to determine basic viscosity in an Ostwald viscometer. Appreciable re-setting occurs if the mix is left to stand for as long as 15 min.

Little has been published, though doubtless much is known, about the effects of the addition of various consistency improvers. Horrall, Epple, Elliker & Brown [1941] claim that lecitho-protein from the soy bean increases viscosity but slightly reduces overrun. When 20 – 25 % sucrose was replaced by cerelose ("corn sugar", from maize) the ice cream melted faster and seemed to have a better flavour: otherwise texture and quality showed no change.

Potter, Deysher & Webb [1949] have compared data for ice-cream mixes and evaporated and condensed milks from a variety of viscometers: torsion pendulum, Brookfield (measures work to stir at constant speed), MacMichael and Majonnier–Doolittle (*vide supra*). Operating under standardized conditions, these instruments are claimed to give interconvertible relative viscosities on an empirical basis.

4. Miscellaneous Uses of Milk and Milk Products

Studies on the effects of addition of milk to flour in bread-making on the rheological properties of doughs hardly fall within the scope of this chapter (*vide* Chap. II). Nevertheless a few important references may be profitably included here. St. John [1927], St. John & Bailey [1929] and Stamberg & Bailey [1942] have worked first on 30 % flour pastes with skim milk, using a filling capillary type of viscometer; and later, on the effects of heat treatment of milk as shown by the polarograph and farinograph. (The latter gives a work/time curve as the dough is mixed at constant speed). Lactalbumin molecules of low molecular weight, with exposed sulphhydryl groups, tend to soften doughs, an effect somewhat analagous to that of cystine and cysteine. These compounds are destroyed by heating the milk. MORSE, DAVIS & JACK [1950a, b] have studied the effects of non-fatty milk solids using a Stormer (rotation) viscometer and a Bloom penetrometer for flour pastes. Strangely enough, sugar decreases gel strength in thick pastes but increases the consistency of thin pastes. In ref. (b) a falling sphere is also used for various foodstuffs: sauces, custards, etc.

WEBB & HUFNAGEL [1946], using a MacMichael viscometer, have studied the effects of the use of various milk products on the "heat stability and viscosity of cream-style foods."

Finally, without it is hoped, infringing too much the territory of Chap. VII, we mention the work of ROSE & COOK [1949]. Carrageenin, a seaweed extract, is used to suspend cocoa powder in milk, probably because quite small quantities of carrageenin produce a very high viscosity. A heat-sensitive casein-carrageenin gel is formed.

The correlation coefficient between the "suspending power" of samples in milk and the viscosity in NaCl soln., is 0.91; hence the latter may be used as an adequate index of the former.

BOGDANOV [1939], as well as measuring the viscosity of milks from various species of animal, has studied Koumiss (fermented milk), which is claimed to have a relative viscosity ~ 1.9 at 25° C. The viscosity is used as an index of quality. Determining the volume-concentration (ϕ) by centrifuging out the protein, Bogdanov applies an equation similar to that of HATSCHEK [1911]

$$\eta_{\text{Koumiss}} = \frac{\eta_{\text{cont. phase}}}{1-\phi^{1/3}}$$

5. Human Milk

Although discussed in another of this series of Monographs (Frey-Wyssling, "Deformation and Flow in Biological Systems", 1952), mention should here be made of the work of WALLER, ASCHAFFENBURG & GRANT [1941] on prenatal human mammary secretions, the rheological aspects of which were studied by SCOTT BLAIR [1941]. It was thought that certain pathological conditions occurring during lactation might be caused by excessive internal pressure promoted by rheological anomalies in the secretions, and that relief could be obtained by the removal of the secretion before parturition. It was found; however, that although there were wide differences in viscosity, even those secretions having the highest viscosities, both pre- and post-partum, behaved in a very nearly Newtonian manner. The "anomaly" theory therefore had to be discarded. The viscosities and their variations with pressure changes were determined in a specially designed U-tube capillary viscometer.

CHAPTER IV

THE CONSISTENCY OF BUTTER

BY

H. MULDER
DAIRYING LABORATORY, THE AGRICULTURAL UNIVERSITY
WAGENINGEN, NETHERLANDS

0. Introduction

The rheological properties of butter are very important in relation to quality. The whole complex of these properties is so characteristic in butter that other substances are often said to have a butter-like consistency.

In the first place it is required that butter should have a good spreadability: it should not be too firm, since, if this were the case, the bread would be broken into pieces when the butter is spread on it; yet butter must have a certain firmness, it must not collapse. Butter should not be extensible, long or tough; however, it is just as well that it should also not have the reverse properties; crumbliness, brittleness, shortness. Butter should not be oily or sticky; when it is tasted, it should not give a sandy or mealy impression to the tongue. When spread, it should not be "dead" but should show some elasticity.

Butter is a natural product whose properties vary to some extent with the season of the year. There is some uncertainty as to the requirements of consistency. It is not always easy to say just what firmness a sample of butter should have since this may depend on the conditions and purpose for which it will be used. In England, for example, the whole contents of a barrel of butter are placed on the counter. The butter must not collapse, but should keep its original shape even at summer-time temperatures of 20° C. In winter, many butters are difficult to spread at breakfast-room temperatures and it would be an advantage if the butter could be spread easily at low temperatures without breaking the bread.

No butters could, of course, fulfil all the desirable conditions perfectly, and at this moment one can only say that butter should be as firm as possible in summer and as easily spreadable as possible in winter.

1. Properties of Butter

1. 1. *The Composition of Butter*

Butter contains more than 80 % fat, some 16 % water, 0. 5 % protein, 0.5 % lactose and lactic acid, 0.1 % inorganic substances from milk and 0 – 3 % salt.

Of the compounds which are present in the solid state, the most important is the fat. The influence of the fat on consistency is complicated. At room temperatures, the butter fat is in a semiliquid state and the butter is spreadable while at the same time having a certain measure of firmness. Not only is the degree of solidification of the fat important, but also the form in which it occurs (dispersed or continuous) and the structure of the solid fat itself.

The direct influence of the proteins on the mechanical properties of butter is probably not of great importance. MULDER's [1940a] experiments show that there is no difference in firmness between butters made from sweet cream and those made from acidified cream.

No influence on the firmness of butter could be found which depended on difference in moisture content. It should be noted, however, that the variations in moisture content are generally so small that it is not supposed that they should cause any appreciable difference in firmness. Moreover, the water in butter occurs in the form of small drops which resist deformations and hence, do not appreciably decrease the firmness of the butter.

MULDER's [1941] experiments have shown that salted butter, which contains relatively large water drops, is less firm than unsalted butter in which the water is generally dispersed in a finer form. This, however, is no proof that the firmness is affected directly by difference in the degree of dispersion of the water.

1. 2. *The Structure of Butter*

Butter consists of a large number of fat globules and water droplets held together by a continuous fat phase. As well as this continuous fat phase, there is a residue of a continuous water phase from the milk. Butter is a kind of gel and it is logical to suppose that its rheological properties are not dissimilar to those of other gel structures. That the structure is important is clearly shown by the difference in rheological properties of ordinary butter and of butter which has been warmed to a temperature of a few degrees below its melting point and then subsequently cooled. This difference in consistency can be observed in everyday life when butter which has been warmed to a temperature high enough to make it spreadable, cools down again to become hard and brittle.

As is the case with other dispersions, the consistency of butter will be influenced by the volume, both of the dispersed phase and of the continuous phase, by the flow properties of the continuous phase, by the deformability of the dispersed phase and by the proportion, form and arrangement of the dispersed particles. None of these factors has yet been satisfactorily studied. KING [1947] made the first estimate of the relationship between the volume of the dispersed phase and continuous phase by counting and measuring the fat globules. The technique, however, is difficult and not very accurate.

The influence of the proportion of fat globules on the consistency has often been reported, but it has not hitherto been really proved that such an influence exists.

The orientation and mutual relationship between the fat crystals will be treated in 1.7.

It must be borne in mind that fat globules are not enveloped in a tough skin giving them a certain firmness like an indian rubber ball, but that the surface layers are very fragile. Any deformation of the butter will cause more or less serious damage to the surface layers of a number of fat globules. The surface layers are only important insofar as they make it possible for the fat globules to exist, and for an inhomogeneous distribution of the triglycerides of the butter fat to be possible.

1. 3. *The State of Crystallization of the Butterfat*

It has already been remarked that the peculiar consistency of butter is caused by the fact that at room temperature this material is in a semi-solid state. The crystallization of the greater part of the fat makes the butter firmer and less spreadable, whereas when the majority of the fat is in the liquid state, the butter is soft and easy to spread. The state of crystallization of the fat depends on its composition and temperature, and on the temperatures to which it has previously been subjected. MULDER [1940b] has proposed a theory concerning crystallization and melting of butterfat to the effect that the fat can crystallize into homogeneous mixed crystals.

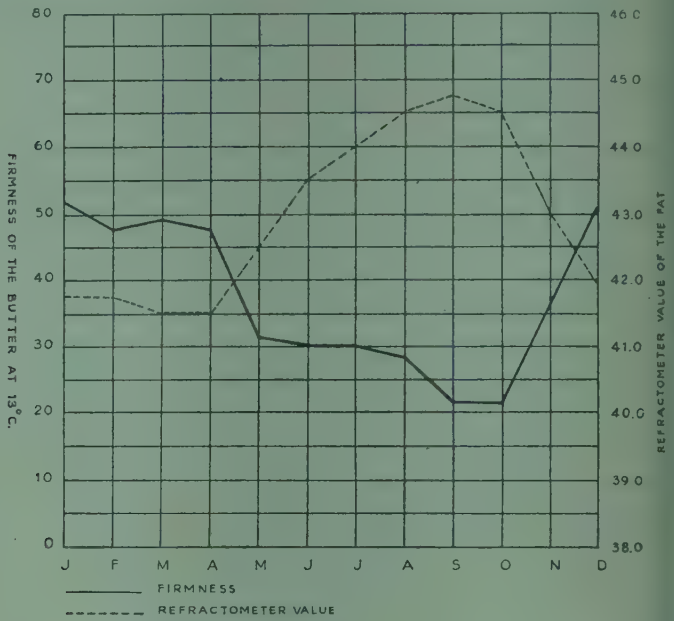

FIG. 1b. Relationship between refractometer value of the butter fat and firmness of the butter; POSTHUMUS [1951].

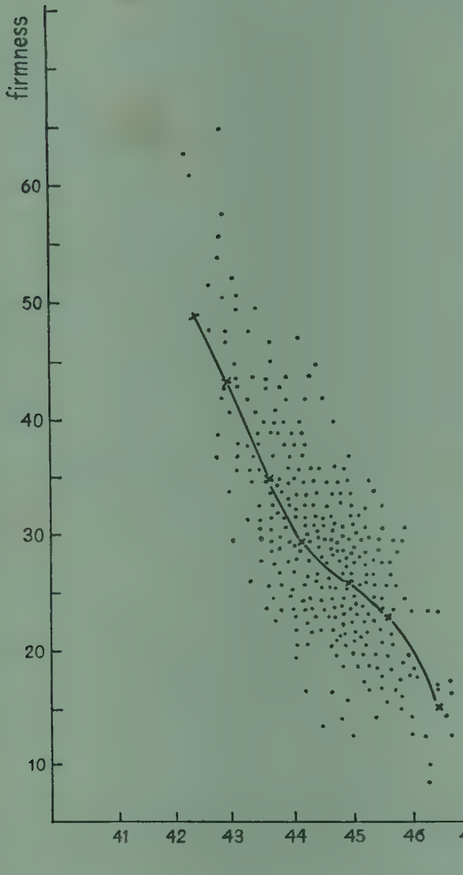

FIG. 1a. Relationship between Iodine Number and Firmness.

The relationship between the firmness of butter and the composition of the butterfat has been studied in many countries. Fig. 1 illustrates this, showing the results of an investigation into the relationship between the iodine number and the firmness of Dutch factory-made butter. The correlations would certainly have been much better had the butters not been made by different methods and in different dairies (KRUISHEER *et al.* [1943]).

Fig. 1b shows to what extent butter fat varies in composition during different seasons of the year and in relation to its firmness over the same period. It is clear that the butter is firmer in winter and softer in summer. This is an unfortunate fact as far as the butter industry is concerned.

Some improvements, however, can be made. The composition of the butterfat depends on a number of factors (e.g. the nature of the feed of the cattle, their state of health, the breed and also individual variations between cows) and some of these factors can be partially controlled. The influence of the feed of the cattle on the composition of butterfat is considerable (BROUWER *et al.* [1943]) and this can be regulated.

Unfortunately, a complete control of the butterfat and hence of the firmness of butter, is not practicable on economic grounds.

The state of crystallization of the fat can be influenced to some extent by the temperature treatment of the cream. This influence is relatively small, but may sometimes be of great importance.

1. 4. *The Temperature of the Butter*

Butter is stored and used at temperatures which lie within the range of the melting and solidification of the butterfat. In some cases, relatively small changes in temperature may cause important changes in the state of solidification of the fat and the consistency of the butter. Fig. 2 indicates the importance of the influence of temperature on firmness and Table 1 shows that this influence is not the same in every case (as a further example, see 1.8, table 10.

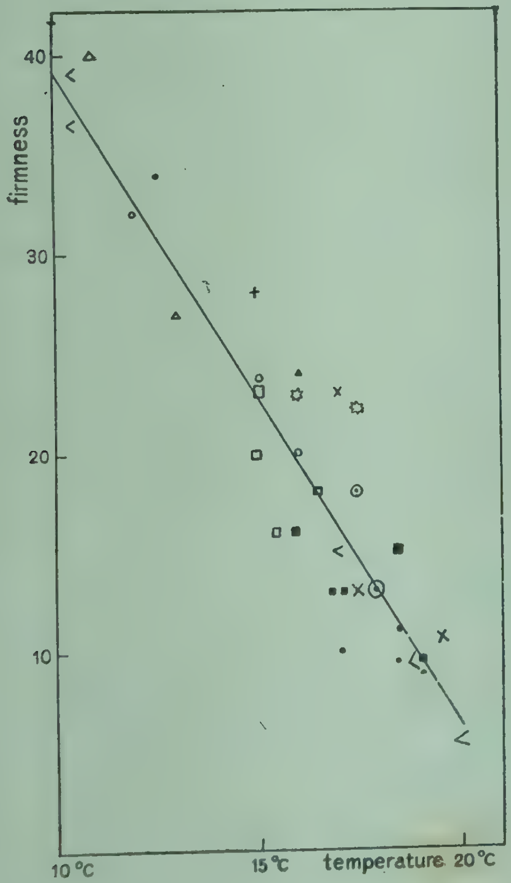

FIG. 2. Firmness of Butter imported into England from Different Countries at the Temperature of Shops and Store Houses.

TABLE 1

Influence of the temperature on the firmness of butter

Temp. treatment of the cream 1)	Firmness of the butter at 2)			
	9.5° C	12° C	13° C	19° C
8–19– 2	40		29.5	2
16–16–14	69		46.5	11
8–13–13	48		46.5	7
19–19– 2	68		53	7
8–13–13 mean of 6 expts.		320 3)		47
19–19– 2		435		42

1. 5. *The Method of Manufacture*

Although the consistency of butter is primarily determined by the composition of the fat, manufacturing methods can also have an important influence in certain cases. It may safely be stated that when the composition of the fat is unsuitable, it is impossible to prepare butter of good consistency, but also, that however ideal the composition of the fat may be, bad methods of manufacture will result in bad consistency. It is thus possible to influence the state of crystallization of the fat and the structure of the butter during the manufacturing process. In studying this, it must constantly be borne in mind that butter shows a time-hardening; a setting process as the result of which the firmness increases enormously.

1. 6. *The Firmness of Freshly-made Butter*

This depends primarily on the state of crystallization of the fat. This state of solidification in its turn, depends on the composition, the temperature and the temperature history of the cream from which the butter has been made.

Fig. 3 and Table 2 show this clearly.

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1) Index of the temp. treatment of the cream: 8–19–2 means that the cream after pasteurization was cooled to 8° C, after 2 hours, was warmed up to 19° C and 5 hours later was cooled to 2° C and kept at that temperature during the night.

2) Determined with apparatus of Kruisheer & Den Herder.

3) Determined with apparatus of Perkins.

TABLE 2

Influence of the state of solidification of the fat on the firmness of the fresh butter

Temperature at which the butter was made and the firmness estimated	Dilatation 0/000 of the cream (from churning temp. — 28° C)			Firmness of the fresh butter from		
	cream 10	19–19–2	8–19–2	cream 10	19–19–2	8–19–2
10° C	160	178	155	20	26	19
13	135	150	132	11	15.5	11.5
17	106	103	94	6	5.5	4

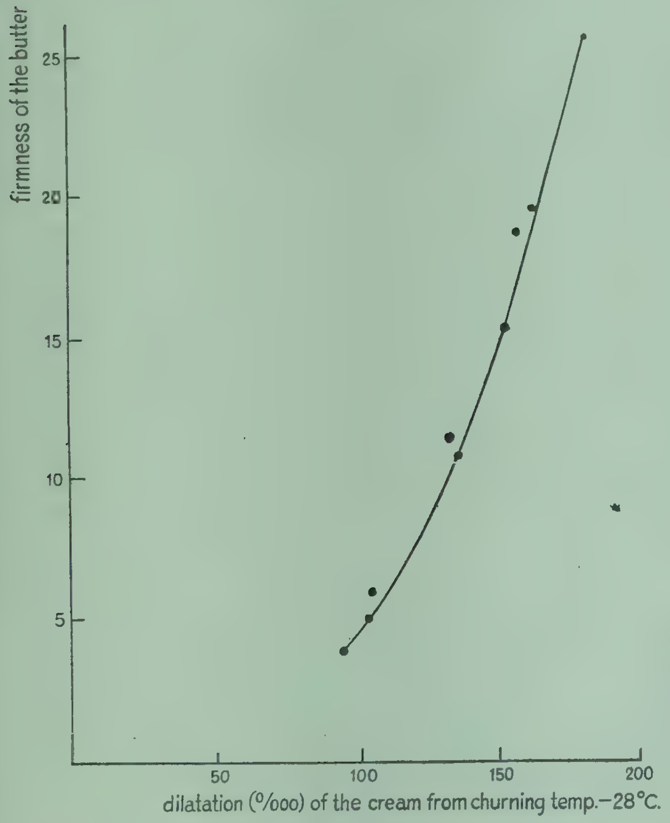

FIG. 3. Relationship between the State of Solidification of the Fat and the Firmness of the Fresh Butter.

1. 7. *The Setting Process*

The setting process is responsible for large alterations in the consistency of butter. In some cases, for example, the firmness increases by more than 2000 %. MULDER [1939] has distinguished two types of process:

(a) a setting, resulting from changes of different type of crystallization,

(b) a setting as a result of thixotropic processes.

Crystallization of the fat. Butterfat can easily be super-cooled and liquid fat often occurs in freshly prepared butter in the super-cooled state. When this super-cooled fat crystallizes, the firmness of the butter increases as the solid fat increases and as skeleton-like structures are formed as a result of the growing together of the fat crystals. An example is given in Table 3.

TABLE 3

Increase of the firmness of butter by crystallization of super-cooled fat

After past. the cream was cooled to	Dilatation 0/000 of the cream (16 – 30° C)	Immediately after working		After 1 week setting at 16° C		
		dilatation of butter	firmness of butter	dilatation of		firmness of butter
				cream	butter	
2° C	136	131	9	137	136	40
16 °C	97	105	3	135	132	48

If, after the crystallization of the super-cooled liquid fat, the butter is re-worked, the crystal structures mentioned above are destroyed. Since there is no more super-cooled liquid fat present, no new structures can be formed during the re-setting. This explains why butter with an elaborate crystal structure (made from cream which has not been cooled to a very low temperature), will soften more on re-working than butter which contains only a limited amount of structure (See Table 4).

TABLE 4

Crystal structures in butter are destroyed by working

Treatment of the cream	Firmness of the butter	
	after setting	after re-working and re-setting
8 – 13 – 13	22.5	12
13 – 13 – 13	28	13
8 – 13 – 13	18	14.5
16 – 16 – 15	26	15
8 – 13 – 13	16	12
16 – 16 – 14	21	12

The influence of a re-crystallization of the fat. This was observed by Mulder [1945] with butter which, after it had been made and stored at a relatively low temperature (13° C), was kept at a high temperature (19° C). As a result of the re-crystallization, the quantity of solid fat decreased and therefore the firmness of the butter diminished (Table 5).

TABLE 5

Recrystallization of the fat

Storing of the butter at 19° C during	Firmness of the butter at 19° C
1.5 hour	7.5
1 day	6.5
2 days	5.5
7 days	5.5

Thixotropy. When the butter which had been kept at a temperature of 10—12° C was re-worked, it became soft and oily; but when after working it was left to itself it became firm again. It is not known exactly what takes place during the setting process but Table 6 shows that butter has thixotropic properties.

TABLE 6

Thixotropic properties of butter

Treatment of butter	Firmness at 15° C
1 week storing at 10–12° C	250
after re-working	73
again 1 week storing at 10–12° C.	200
after re-working	70
again 1 week storing at 10–12° C.	171

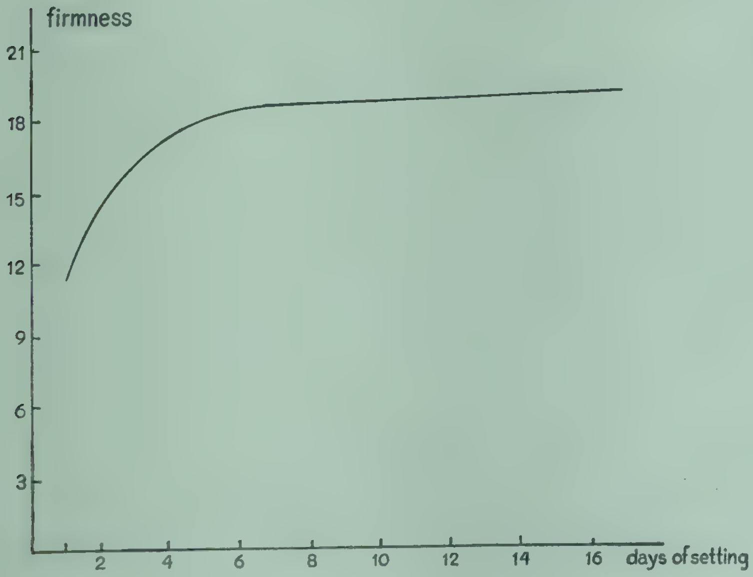

FIG. 4. The setting process is an asymptotic one.

The setting process is an asymptotic one: under certain circumstances, for example at low temperatures, it may continue for weeks and months (Fig. 4; Table 7).

TABLE 7

Influence of the time on the setting process

Time	Temperature of setting			
	— 70° C	0° C	4—5° C	16° C
0,5 day	—	—	—	9,5
1 day	8	9	10,5	14
6 days.	8	—	—	14
10 days.		9,5	13	16
42 days.		13	17	17
97 days.		14	20	
174 days.		15	20	
448 days.			24	

The influence of the temperature on the setting. This is important because the particles of the butter need a certain freedom of movement to form structures. At a low temperature, at which the greater part of the fat is in the solid state, the freedom of movement is small and consequently the velocity of the setting process is also small. It is even possible to freeze the setting process. This is in direct contradiction to older theories according to which the most rapid setting is obtained at a low temperature (See Table 8; Fig. 5).

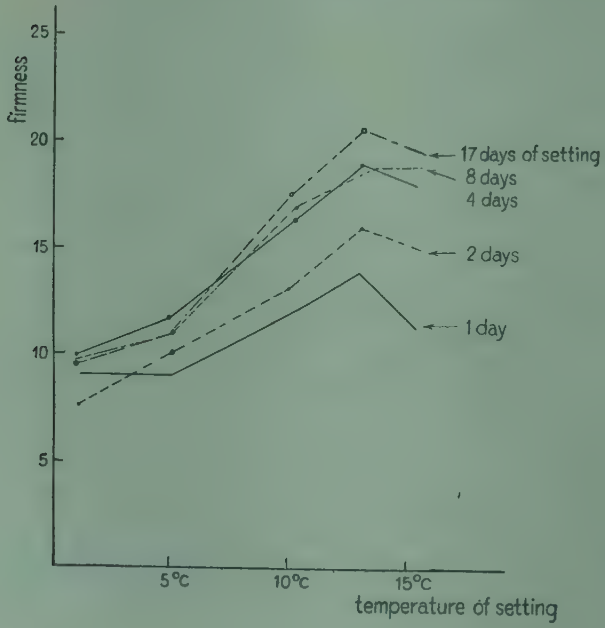

FIG. 5. Influence of the Temperature on the Setting.

TABLE 8

Influence of the temperature on the setting process

The butter was stored during 1 week at (° C)	Firmness of the butter	
	16° C	19° C
0	15	5
4–5	16	6
9	38	12
13	38	13
16	27	12

When freshly made and worked butter is raised to a relatively high temperature, an irreparable loss in firmness takes place. Hitherto, this loss could not be explained; table 9.

TABLE 9

Influence of the temperature on the first part of the setting

Treatment of butter	Firmness at 19° C
1 week at 2° C + 1 week 19° C + 1 week 19° C . .	18
1 week at 19° C + 1 week 2° C + 1 week 19° C . .	13

So far, we have considered changes in firmness related only to the setting process, but there are other alterations in rheological properties which must be considered. Immediately after working, the butter is an oily mass which gradually becomes firmer and shorter as well as less tough and sticky, as setting proceeds. If large numbers of crystal groupings are formed, the butter will become very short and brittle.

In summer, the maximum firmness is required and it is therefore at this time of the year that the formation of large numbers of strong crystalline structures should be promoted in the packed butter. In winter, on the contrary, the formation of crystalline structures should be prevented as much as possible, since these structures would tend to make the butter brittle and unspreadable. A number of methods designed to effect this have been discussed by MULDER [1940b].

1. 8. *Variations of temperature*

This may well have a marked influence on the consistency of butter which may be either increased or decreased. The butter may also become brittle as a result. For example, a high temperature will cause the solid fat partly to melt and re-crystallization can take place. When the temperature is afterwards lowered, the liquid fat can re-solidify. Crystal structures are thus built up, which increase firmness and make the butter shorter and possibly even brittle (MULDER [1945]; Table 10)

TABLE 10

Influence of variations in temperature on the firmness of butter

Treatment of butter	Firmness of butter	
	13° C	19° C
the whole time at 13 °C	21.5	8
4 days at 13° C + 1 day at 16° C + 5 days 13° C .	25	8
4 days at 13° C + 1 day at 19° C + 5 days 13° C .	28	6.5
4 days at 13° C + 1 day at 22° C + 5 days 13° C .	29	5.5

2. The Estimation of Rheological Properties

2. 1. *Organoleptic Method*

In studying the consistency of butter, we are concerned with a complex of rheological properties. Nevertheless, when butter is judged under technical conditions and by the trade, the consistency is generally expressed by a single figure, although this is often amplified by comments such as "brittle, tacky, soft", etc. The consistency is judged by pressing with the thumb or with a spatula into the butter (and especially by pressing on to a plug of butter in the trier), by spreading out the butter or by pressing it between the tongue and the palate in the mouth. By this means, it is possible for the judge to gain impressions of quite a number of rheological properties such as firmness, spreadability, brittleness, elasticity, etc., although their differentiation is often not consciously appreciated by him. The trained judge is highly skilled in detecting small differences in consistency (see IV, 2.3, fig. 8). It is impossible to exaggerate the importance of his capacity to judge the whole complex of consistency-factors, even though he may not be aware precisely of what he is judging, nor can he assess each component separately. For the butter manufacturer, the salesman and the consumer, it is the whole complex of properties which is important: analysis into separate components is not of interest.

2. 2. *Objective Mechanical Methods*

Although the organoleptic method has many advantages, there are also disadvantages, especially in that it is essentially a subjective method. Many workers have tried to find objective mechanical methods. At first these were purely empirical, but later modern methods of rheological research have been tried with some success by many authors.

Hitherto, however, fully satisfactory results have not been obtained. This is partly due to the fact that in most cases an analytical approach has been used, in an attempt to estimate the rheological properties separately and under different specific conditions. Since the consistency of butter is such a complex concept, this analytical method could not have a very direct practical value.

In most cases the problem was restricted so that only one aspect of consistency was studied and firmness was generally chosen. Undoubtedly firmness is one of the most important factors in consistency and other properties will certainly show a high correlation with it. It is reasonable to suppose, for example, that a good correlation will exist between firmness and spreadability, the latter being defined in terms of the force required to spread the butter under standard conditions. On the other hand, there will be little connection between firmness and certain aspects of the manner in which the butter behaves when spread on bread, for example, whether it forms a homogeneous layer or crumbles, etc., since this behaviour depends not only on the force required to spread the butter, but also on such properties as tackiness, shortness and brittleness.

Meanwhile it is not easy to estimate firmness and it is difficult even to suggest a satisfactory definition for this property. Possibly the resistance which the butter offers to a shearing stress should be called firmness, but this definition would hardly be adequate, since the nature of the stress is itself not without influence. A small stress operating over a long time may sometimes cause a greater deformation than a higher stress operating only for a short time.

Depending on the conditions under which the butter is subjected to the deforming force, a distinction can be made between the firmness of butter when it is spread, its firmness when standing on the counter and its firmness in relation to organoleptic tests. There may well be a relationship between these three types of firmness and it might be sufficient to estimate only one of them; but so long as no definite experiments have been carried out to settle this point, the three types of firmness should be strictly distinguished from one another, a point which is often overlooked.

Apart from methods of determining rheological properties by means of objective tests, the possibility of expressing the data in c.g.s. units has been studied. This is certainly a correct procedure but here also, many mistakes have been made. For example, most viscosity data cannot be regarded as absolute, but rather as of an arbitrary character. It is therefore not justifiable to compare them directly with one another, even though they are, in fact, expressed in c.g.s. units.

2. 3. *Penetrometers*

The first apparatus to be used in the rheological study of butter was the penetrometer.

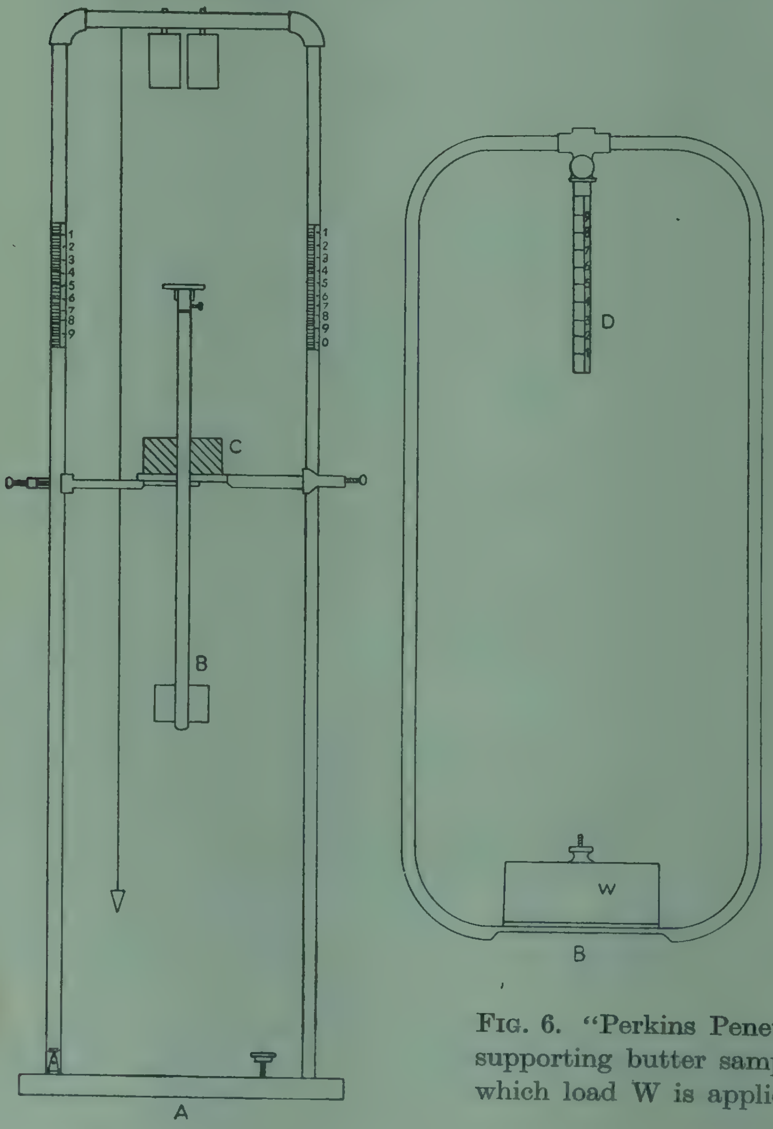

FIG. 6. "Perkins Penetrometer". A is stand supporting butter sample C; B is frame by which load W is applied to needle D.

BRULLÉ [1893] rested a vertical rod on a butter sample and loaded it with weights until it penetrated the butter rapidly (oleo-grammeter).

SOHN [1893] described a similar apparatus. MEYERINGH [1911] used a penetrometer following the studies which KISSLING [1891] had made on railway grease. This author stressed the importance of the nature of the material from which the rod is made in influencing the data. He found for one sample of butter, for example, that a consistency figure of 52 was obtained when the rod was made of glass, but that the figure fell to 18.5 using brass.

Woods and Parsons (see PERKINS [1914]) caused a glass rod to fall into a butter sample and determined the depth of penetration. The penetrometer designed by PERKINS [1914] has been fairly widely used

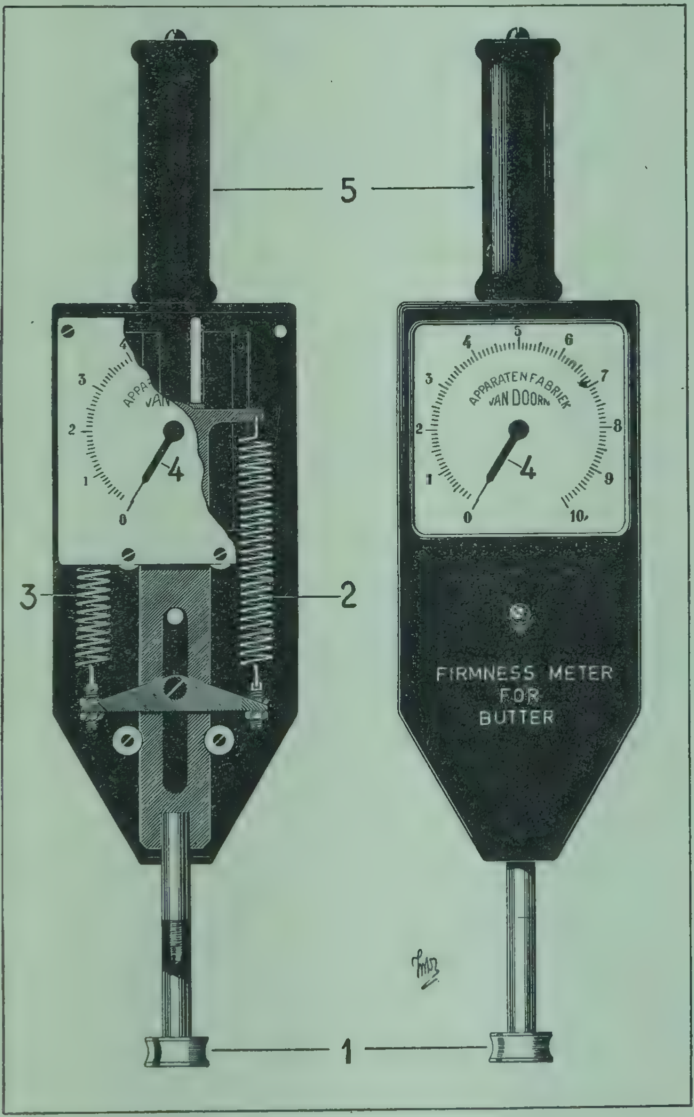

FIG. 7. Firmness Meter of Kruisheer and Den Herder.

(Fig. 6). A cylinder of metal is dropped from a definite height into the butter and the penetration is measured. The volume of butter displaced by the rod is taken as a measure of "hardness". Rods of varying diameter and weight can be used: Sirks points out that the hardness figures obtained depend on the nature of the material of the rod. This apparatus has been used by Perkins. Haglund, Wode & Olsson [1930], van Dam [1938]; Mulder [1938]; Adriani & Tamsma [1941]. Lyons [1936] constructed a similar apparatus.

The author is aware that other instruments based on the same principle have been constructed and used in practice for some time, but since no details have been published, there is little point in discussing them.

Kruisheer, den Herder, Krol & Mulders [1938] tried to relate firmness as estimated by judges, organoleptically (see 2.1) to an objective test. At their suggestion, an apparatus was constructed to determine the force required to press a stamp (area 4 cm^2) into butter at a rate of 1 cm in 30 secs. The apparatus resembles an inverted spring balance (see Fig. 7).

Fig. 8 shows the correlation between data obtained from the apparatus and the estimates given by the judges after pressing with the thumb on the butter. The correlation is remarkably high and such deviations as there are result as much from imperfections in the organoleptic method of judging as from those in the apparatus. The accuracy with which the judges can assess the firmness of butter is striking.

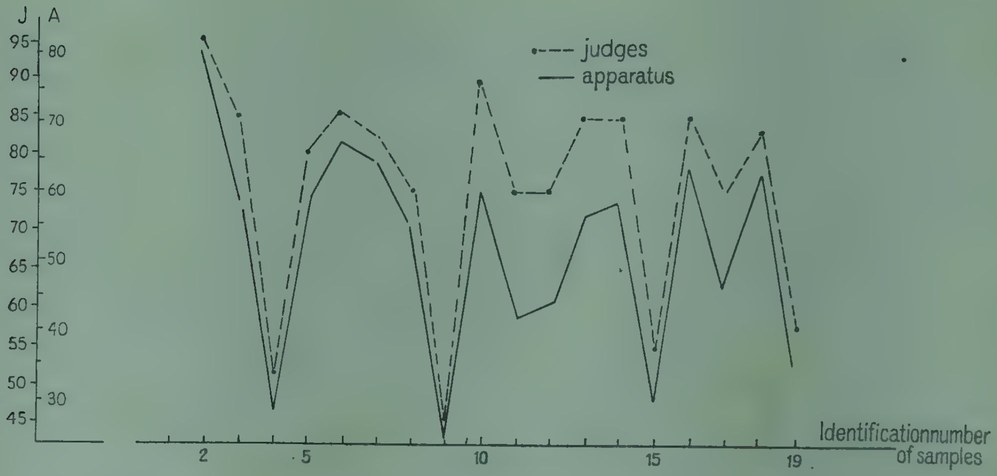

Fig. 8. Correlation between the Figures given by Judges and Figures from the Apparatus.

Kruisheer, den Herder and their co-workers also investigated what rheological meaning could be attached to the data obtained by their apparatus. They loaded a stamp (area 4 cm^2) with different weights and determined the penetrations into the butter after 30 sec. Yield-values calculated from these observations were about 0.7 times the data obtained from the apparatus described above.

From these data one may conclude that both with the apparatus of Kruisheer & den Herder and also with the subjective thumb test, a type of yield-value can be determined. Since in both methods, an increasing stress is applied to the butter, this supposition is even more likely. Kruisheer & den Herder, however, were right not to express the firmness as a yield-value. One reason for this is that the theoretical yield-value cannot be determined in absolute units and depends upon conditions of measurement, for example, when the area of the stamp is doubled, the firmness figure does not become twice as large but only 1. 7 times as large. Moreover, the "firmness figure" cannot be regarded as a yield-value since in the experiment, the stamp has a finite velocity of 1 cm in 30 sec. and the load required to produce this rate of penetration must be greater than the yield-value. Since there is a relationship between the yield-value and the pseudo-viscosity (see page 120), one could express the firmness almost as well in terms of viscosity as in terms of yield-value. The apparatus of Kruisheer & den Herder is very easy to handle and gives good reproducible figures which clearly differentiate different butters. The test is a rapid one and the sample is not damaged since no test pieces need to be removed, the experiment being done on the butter in bulk. In the Netherlands, the method of Kruisheer & den Herder has been accepted officially (Fig. 9).

Mohr & Wellm [1948] used a penetrometer to determine the so-called "Kegelfliesspunkt" and the "Kugelfliesspunkt" (Cone yield-value and sphere yield-value) (Fig. 10). These authors measured the loads needed for the penetration of a cone (height 2 cm, base 4 cm^2) and of a ball (radius 2 cm). At the start of the penetration, the rate is higher than it is later when the penetrometer comes into contact with an ever increasing surface of the butter. Finally, an equilibrium is reached and the rate of penetration approaches zero. The layer of the butter which is in contact with the body of the penetrometer has reached its yield-value at this stage, thus:

$$\text{Yield-value} = \frac{\text{weight}}{\text{Area of contact of penetrating body}}$$

$$\text{or } F_{\text{Cone}} = g/h^2 \qquad F_{\text{Sphere}} = g/h(4-h)$$

(Where h = depth of penetration.)

The test is a slow one since it takes about 6 hours for the rate of penetration to approach zero, hence, the method is not of much use in practice. Moreover, the butter often cracks. For this reason, Mohr and Wellm proposed a penetration time of about 60 sec. provided that in this time the penetration does not exceed 1 cm. In general, the data found by this quick method agree well with those obtained from the more accurate method requiring a penetration time of about 6 hours, but there were occasions on which differences as great as 19 % occurred. The method of Mohr and Wellm has the advantage that the yield-values obtained are almost independent of the magnitude of the loads on the penetrometer (see Table 11). Moreover, the data from the cone agree well with those from the sphere (see Table 12).

Mohr and Wellm preferred the cone to the sphere since the penetration can be determined with greater accuracy with the former method. A satisfactory differentiation of butter samples in terms of yield-values can be made, since the figures for the yield-values range from 0.04 to 1 kg/cm².

TABLE 11

Influence of load on the cone yield-value (Mohr & Wellm)

Experiment No.	Weight	Penetration (cm)	F_{Cone}, g/h^2
1	250	0,688	0,168
	500	0,943	0,168
2	250	0,736	0,147
	500	1,016	0,154
3	1000	0,829	0,462
	1500	1,062	0,426
4	500	0,643	0,385
	1000	0,929	0,369
5	250	0,538	0,275
	500	0,783	0,259

TABLE 12

Correlation between cone yield-value and sphere-yield value

Cone yield-value	Sphere yield-value	Cone yield-value	Sphere yield-value
0,25	0,24	0,086	0,091
0,20	0,16	0,078	0,067
0,15	0,12	1,11	0,94
0,15	0,14	0,072	0,056
0,17	0,15	0,17	0,12
0,17	0,14	0,074	0,049
0,15	0,11	0,049	0,038
0,12	0,093		

2. 4. *Plastometers*

One of the first applications of modern rheological methods to the study of the consistency of butter was that of DAVIS [1937]. He loaded a cylindrical piece of butter with different weights and determined the deformations, both under load and after the load had been removed (Fig. 11). The permanent deformation was used to calculate a viscosity defined as the shearing stress, divided by the rate of deformation, and so expressed in c.g.s. units. From the recovered deformation, Davis calculated a modulus of elasticity. The viscosity and elastic modulus taken together were considered as a measure of

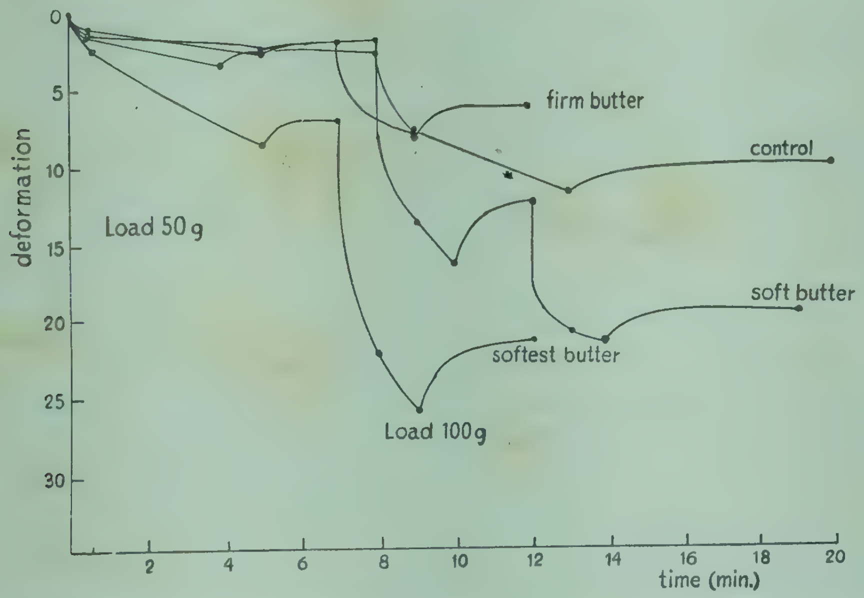

FIG. 11. Deformation of Cylinders of Butter under Load and after the Load had been removed.

firmness, the modulus defining the elasticity and the ratio of viscosity to modulus (relaxation time), defining "springiness". The correctness of these definitions is questionable.

Scott Blair [1938] also estimated an arbitrary viscosity but he was well aware of the difficulties involved. He rightly argued that even for true liquids, certain standard conditions have to be stipulated (e.g. temperature), and that for a material like butter, it is allowable to quote a viscosity in absolute units, provided that the conditions of stress and deformation are specified. When these conditions vary appreciably during the determination, a mean viscosity must be given. Scott Blair constructed a simple apparatus (Fig. 12) in which cylindrical test pieces of butter (diameter 4 cm and height 2 cm) were loaded by means of a weight, and the time required to produce a strain of 0.5 was determined. This strain involves a reduction in the height of the cylinder to 1.21 cm. From this figure, a pseudo-viscosity can be calculated quite simply — $\eta = 0.01896$ Wt; (η = viscosity; W = weight

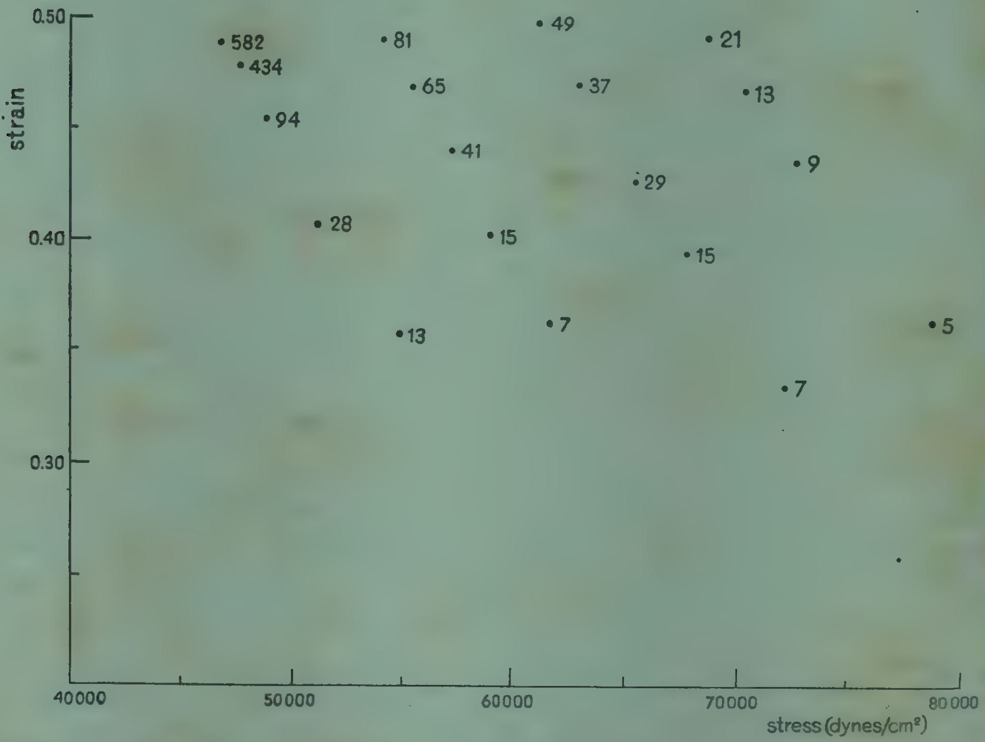

Fig. 13. Different Cylinders of one Sample of Butter under varying Conditions of Compressing. The Four Sets of Points correspond to Loads of 6,5; 7,5; 8,5 and 9,5 lb.

in pounds; t = time). Elastic properties and any possible yield-value are neglected. This does not make any difficulties with the calculation since, according to MULDER [1940b], there is a proportionality between pseudo-viscosity and the yield-value (see 2.8.). During the compression, the diameter of the cylinder of butter increases and Scott Blair uses for his calculations the mean rate of shear. The method has the disadvantage that with these big deformations, cracks often appear in the cylinder of butter. In Fig. 13 are shown the data from different cylinders of one sample of butter under varying conditions of compression. The four sets of points correspond to loads of 6.5, 7.5, 8.5 and 9.5 lb. from left to right respectively (i.e. from about 3 to 4.5 Kg). The calculated figures for viscosity rise enormously with rising strain for any given stress and, at least for higher strains, fall rapidly with rising stress at constant strain. From this, it clearly follows that the figures are arbitrary. Although Scott Blair's apparatus has not found practical application, his work has been of importance, since it has served as a basis for the work of many other scientists. For example, DOLBY [1941] used the apparatus designed by Scott Blair. According to him, the figures are not sufficiently reproducible to indicate small differences in firmness. Most of the difficulties originated as a result of cracks formed at high compressions. Dolby explains that this is a consequence of a laminar structure in the butter but he does not prove his supposition. Probably, the butter which he used was too firm for the measurements. Any butter will crack if it is compressed at such low temperatures that it is firm and brittle. The cracks occur mainly along the lines of principle shear stress.

MOHR & WELLM [1948] have also estimated a kind of arbitrary viscosity using a parallel plate plastometer designed by Höppler (cylindrical test-pieces, area = 4 cm², height = 2 cm). Viscosity figures were calculated according to Scott Blair's method. Mohr and Wellm also pointed out that the viscosity rises with the deformation during the course of the experiment and that it often falls suddenly as a consequence of "Blockfliessen" (bulk-flow). One is therefore obliged to use mean values and it is not possible to calculate a true viscosity. In some cases duplicate observations with the same butter differed by 20 %; and it is therefore necessary to make replicate tests. However, the method gives a reasonable differentiation between butter samples, since the accuracy is of the order of 5 % and the figures for consistency differ from 1.5 — 20 megapoises.

Parallel plate plastometers had been used previously by Hunziker, Mills & Spitzer [1912] and by van Dam [1927], see Fig. 14.

However, at the time when this work was done, modern rheological theory had not yet been developed and the apparatus used was purely empirical. Hunziker *et al.* loaded cylindrical pieces of butter for 20 sec. with different weights and calculated by interpolation what the deformation would have been for a weight of 300 g. Van Dam pointed out that the deformation was not proportional to the load.

Under this same heading may be included the crushing method developed by Templeton & Sommer [1930] for processed cheese and also used by Weckel [1939] for butter. The load required to compress a cube of butter (2.5 cm^3) to half its height is determined. Coulter & Hill [1934] used a similar apparatus for compressing a cube of butter to 2/3 of its height (Fig. 15).

Mention may also be made of the apparatus of Pasveer [1939] in which cylindrical test-pieces of butter are compressed by means of a weight falling on them. This is a typical empirical method.

2. 5. *Cutting Methods* (*Sectility*)

Mohr & Oldenburg [1933] determined the time required to cut a piece of butter under standard dimensions of sample, load, etc. using a metal wire. This time was taken as a measure of firmness. Later, Mohr & Baur [1939] used a constant rate of cutting. Mohr &

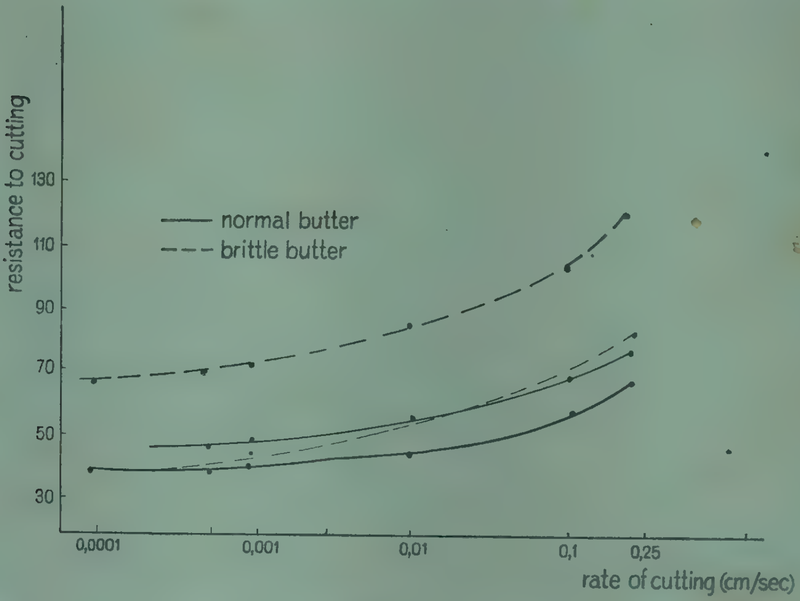

Fig. 16. Relationship between Rate of Cutting and Resistance.

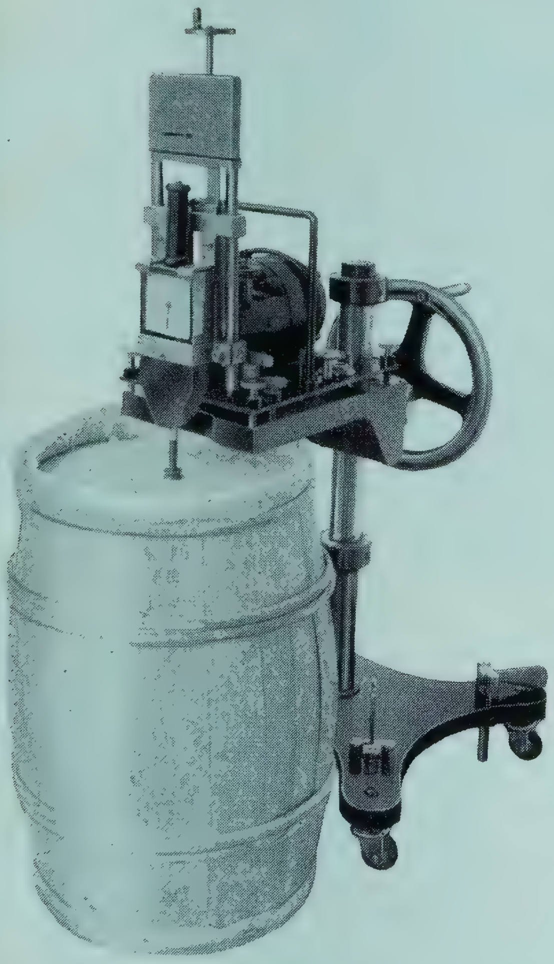

FIG. 9. Motor Driven Firmness Meter used by the Netherlands Butter Inspection.

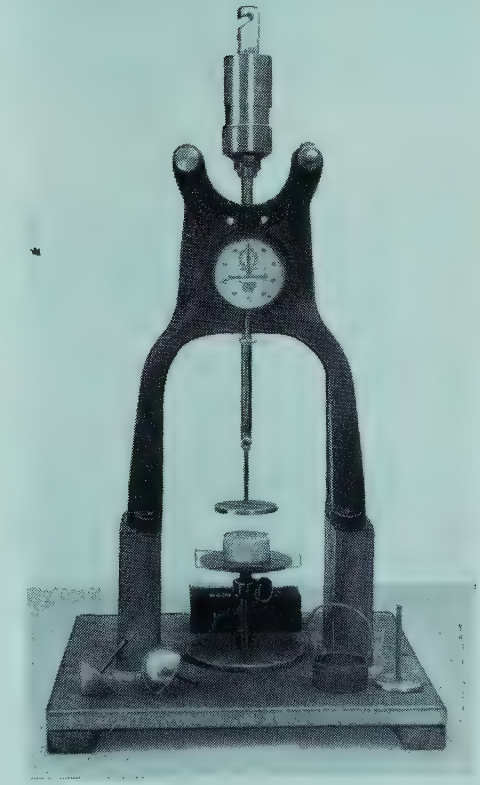

FIG. 10. Apparatus of Mohr & Wellm for estimating the Cone Yield-Value and the Sphere Yield-Value.

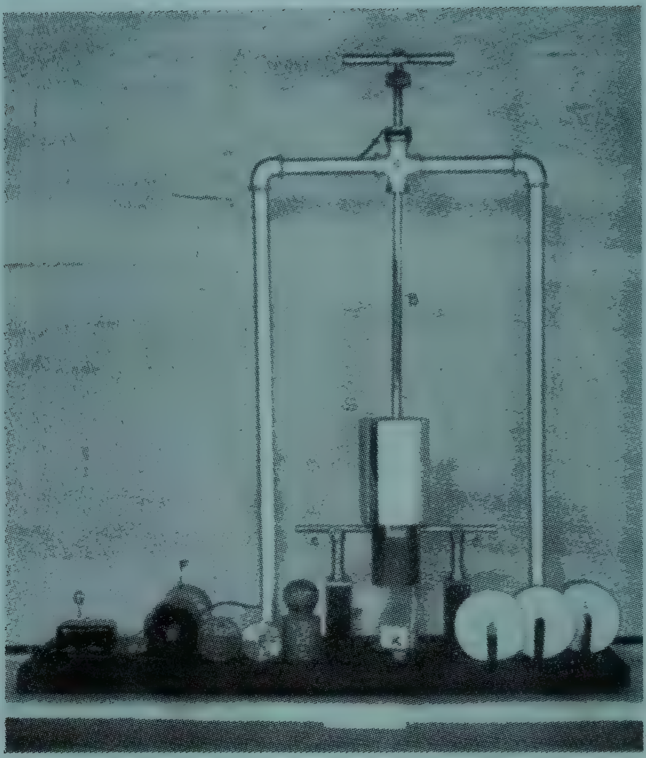

Fig. 12. Apparatus of Scott Blair (from: the Journal of Dairy Research, **9** (1938) 210).

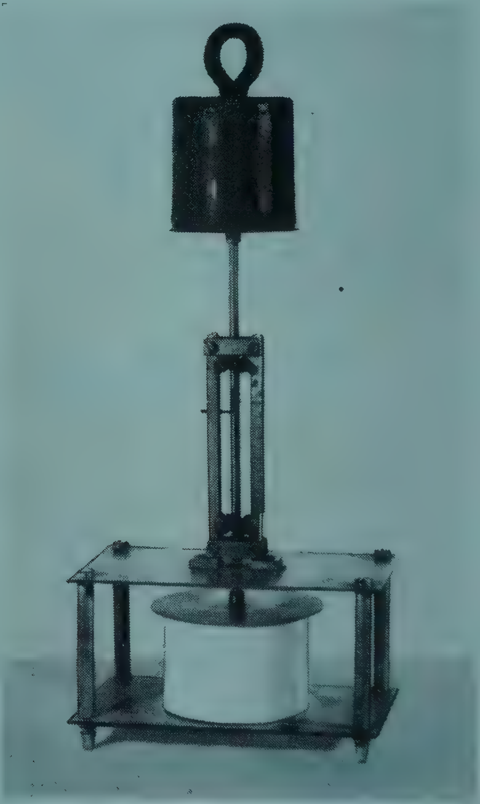

Fig. 14. Firmness Meter of Van Dam.

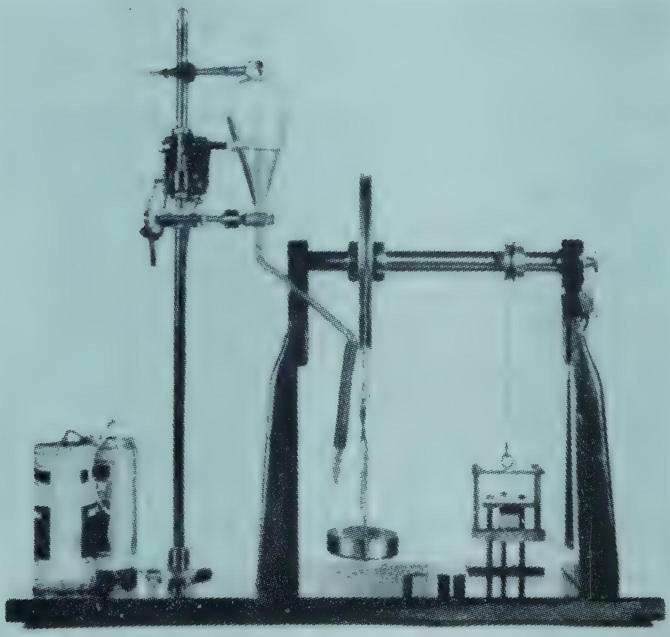

FIG. 15. Apparatus used for Hardness Determinations (Coulter and Combs).

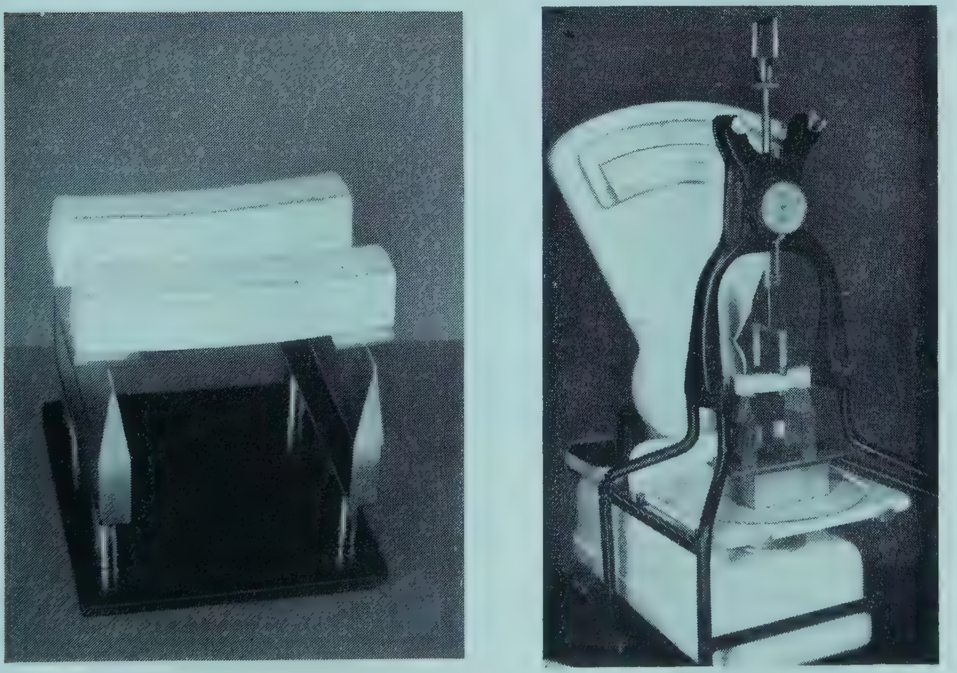

FIG. 20a-b. Apparatus of Mohr and Schulz for estimating the Sagging of Butter.

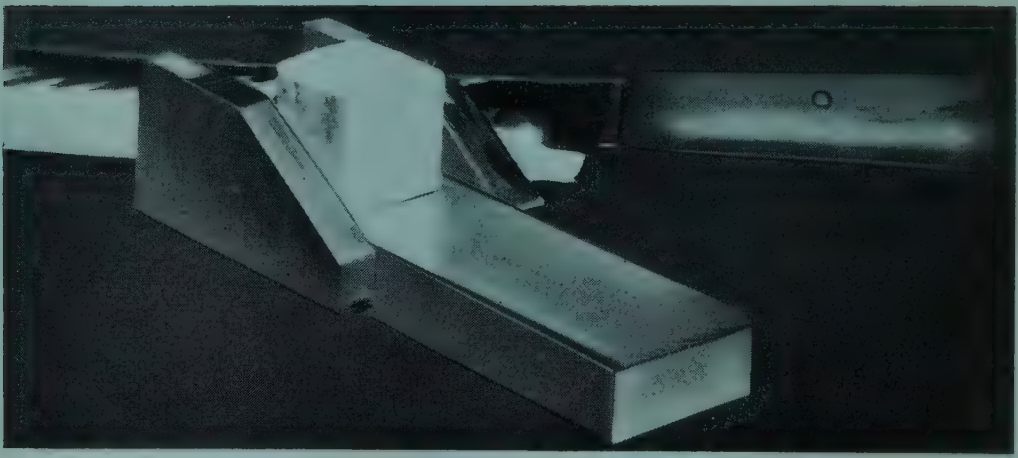

FIG. 21. Judging the Spreadability of Butter (Coulter and Combs).

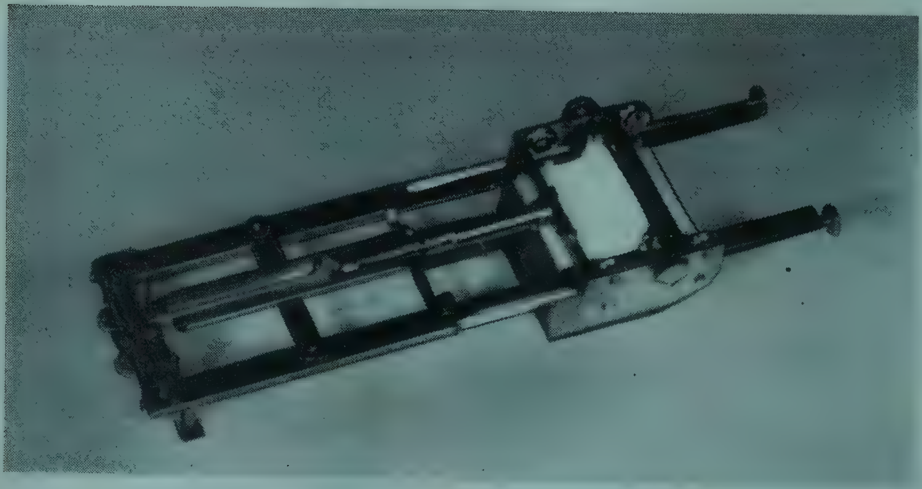

FIG. 22. Spreading Apparatus of Mohr & Häsing.

SCHULZ [1948] further improved the apparatus by introducing a balance to measure the force required to cut the butter. These authors studied the relationship between rate of cutting and resistance (Fig. 16). If the rate of cutting is reduced, the resistance decreases: with increased rates of cutting, it increases. With butters which are brittle and difficult to spread, the increase is greater than with normal butter, but the difference is so small that it is practically impossible to draw from it any conclusions about the structure of the butter.

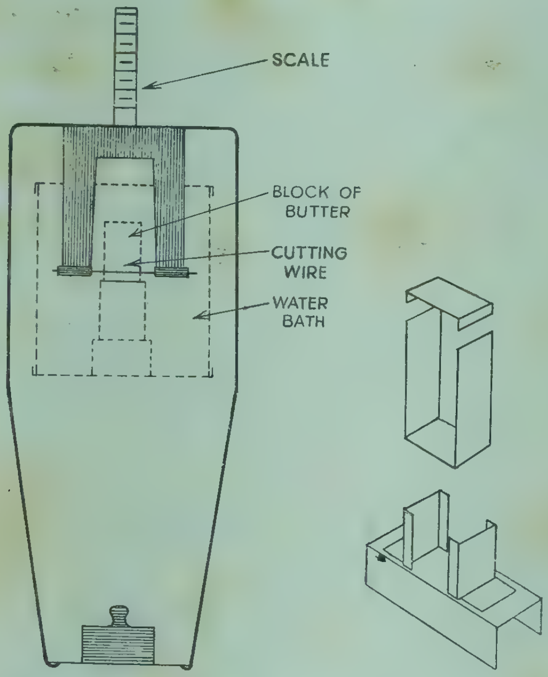

FIG. 17. Cutting Apparatus of Dolby.

DOLBY [1941] constructed an apparatus to cut a butter sample by means of a wire provided with a hanging weight (Fig. 17). According to him, the load required for any given rate of cutting is proportional to the viscosity. In order to support this supposition, he determined the firmness of 50 samples of butter by Scott Blair's method and also with his own cutting apparatus. The results are given by Fig. 18. The figure shows that there is a proportionality between the data given by the two methods. Scott Blair expresses firmness in viscosity units; Dolby did likewise but derived his "viscosity" by multiplying Scott Blair's figures by the proportionality factor. In the writer's opinion, Dolby over-values the use of c.g.s. units (see p. 118). The load required to produce a certain rate of cutting is proportional to the

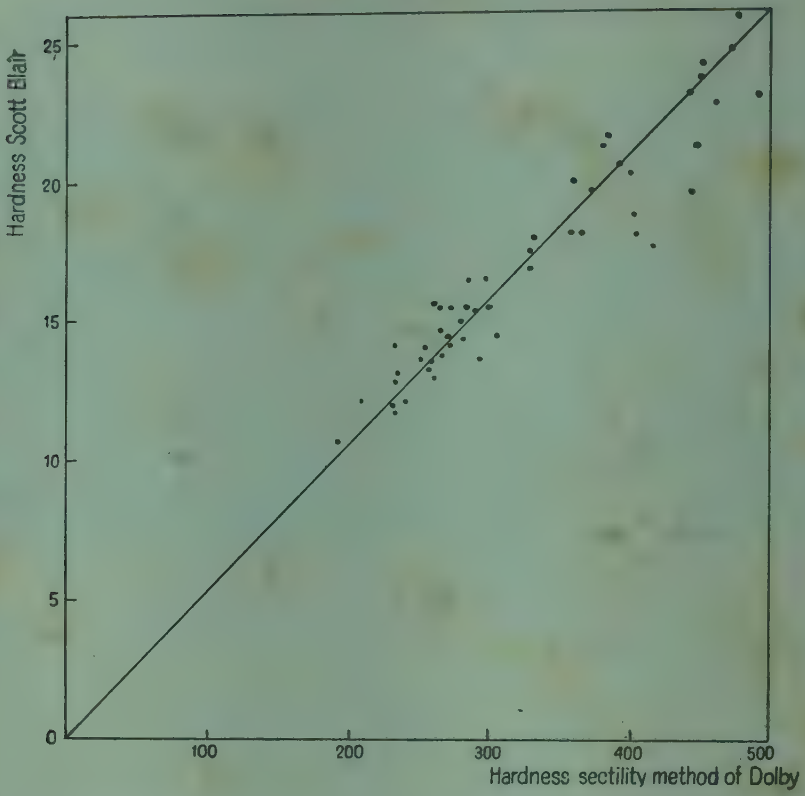

FIG. 18. Relationship between Figures for Hardness obtained by Scott Blair's Method and by the Method of Dolby.

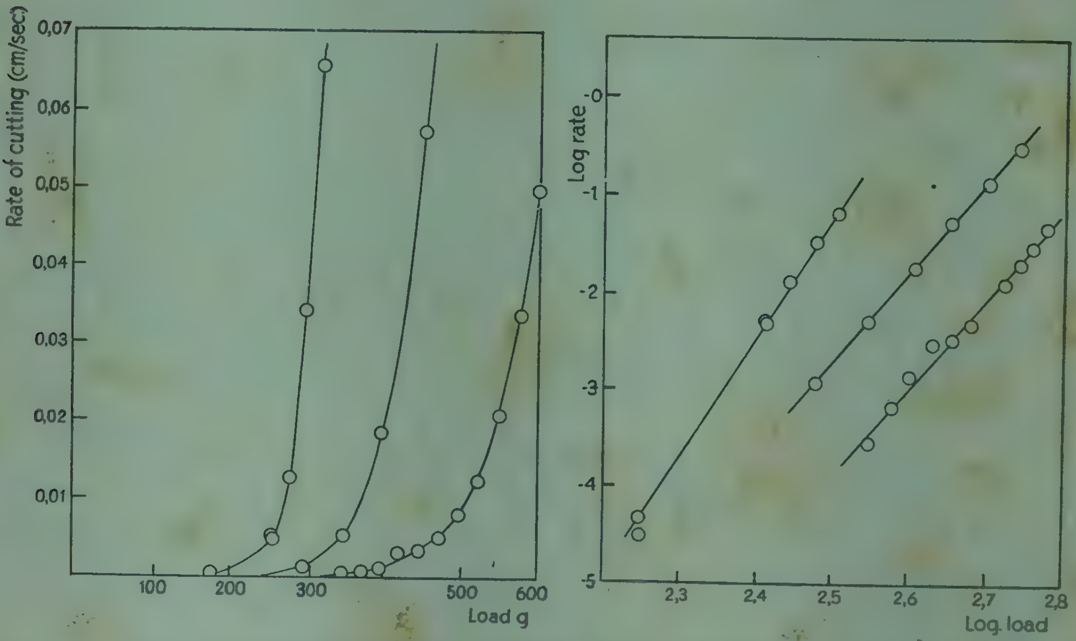

FIG. 19a-b. Relationship between Rate of Cutting and Load.

diameter of the wire and to the length of the contact between the butter and the wire. Fig. 19a shows the connection between the load on the wire and the rate of cutting at a temperature of 12.5° C; Fig. 19b shows the log/log curve. From the fact that the log/log curve is linear, Dolby concludes that butter has no yield-value and is a liquid rather than a solid, and that at all loads, however small, there will be some flow if sufficient time is allowed to observe it. In drawing this conclusion, Dolby forgets the presence of a constant: in his diagram he has moved an axis. Dolby is correct when he says that butter has a practical yield-value; indeed, in view of the results of his experiments it would be hard for him to deny this.

Coulter & Combs [1936] used a similar method but instead of one wire, their apparatus was provided with a number of wires. In Sweden, Wode has also constructed a cutting apparatus but no details have yet been published. Weckel [1939] has determined cutting resistance by quite a different method. He expressed the slicing resistance as the weight of mercury in grams needed to draw a 6.0 cm spatula completely through a core of butter 20 mm in diameter at a temperature of 6.7° C.

2. 6. *Sagging Beam Method*

This method was developed by Leighton, Leviton & Williams [1936] for ice cream (see Chapter III) and has been applied by Coulter & Combs [1936] to butter. A cylindrical piece of butter is supported by its ends in a horizontal position at a temperature of about 26° C and the rate of sag is determined (actually the time required to sag by 5 cm). This sagging time is compared with the capacity of the butter to maintain its shape. Mohr & Schulz [1948] have also made use of this method and have improved it substantially, using it in two different modifications (Fig. 20). First, they measured the sagging of a piece of butter under its own weight after 6 hours at 20° C (test piece 2 × 2 × 8 cm). This they called "Formfestigkeit" (rigidity of form). Secondly, they measured sagging under load, determining the amount of sag at which a bar of butter cracks, to an accuracy of about 10 %. The method could not be used for butters having a high air content nor for soft summer butters. At high temperatures and when the butter is soft, its bending under its own weight becomes important and the accuracy of the method falls to about 20 – 40 %. Mohr and Schulz attempted to relate the figures obtained by these methods to shortness and brittleness.

2. 7. *Spreadability*

Most butter is used for spreading on bread. It is unsatisfactory when the butter is too firm and the bread may break into pieces when spread. Spreading is a complicated process and it is not only the force required to spread which is important but also the brittleness and stickiness of the butter, and the properties of the bread and of the knife. Following the work of GRIFFITHS [1931], VALENTINE & SARGENT [1935] estimated an "extrusion pressure" i.e. the pressure required to force the butter through a narrow orifice. COULTER & COMBS [1936] laid more stress on the way in which butter spreads (i.e. its crumbliness,

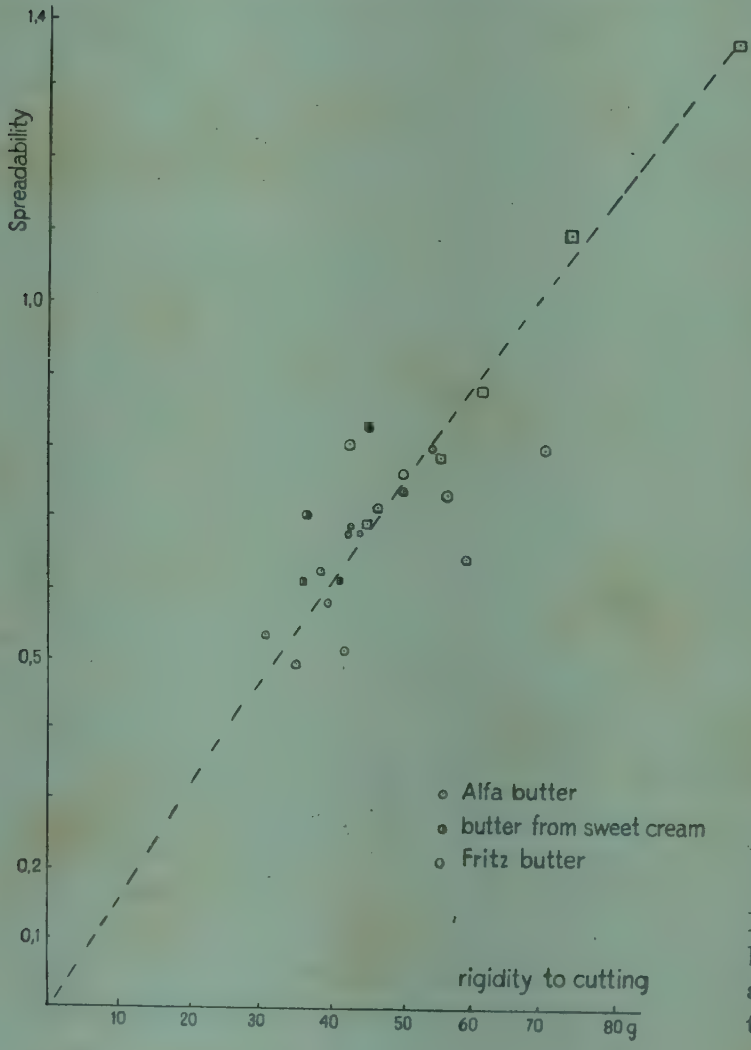

FIG. 23. Relationship between Spreadability and Rigidity to Cutting.

stickiness, etc.) than on the force needed to spread it. In their experiments they spread a cube of butter with a knife and, in order that the angle of shear should always be the same, the passage of the knife was guided by two parallel sloping surfaces between which the sample was placed (Fig. 21). The appearance of the butter after spreading was judged but it is naturally difficult to express such a judgment in objective figures.

MOHR & HÄSING [1949] determined the force required to spread butter. They spread a layer 2 mm thick with the aid of a knife placed perpendicular to the direction of spreading (Fig. 22). There would have been no point in carrying out these experiments at high temperatures, since under such conditions there would have been little differentiation of the samples. Mohr and Häsing worked at a temperature of 15° C. Fig. 23 shows the relationship between "Schnittfestigkeit" (rigidity to cutting) and spreadability. The relationship is approximately linear.

2. 8. *Relationship between various Methods*

In most cases, the properties which are determined by the different methods are essentially different, even if this is not apparent from the way in which the data are presented. Thus DAVIS [1937] calculated his viscosities from non-recoverable deformations, whilst SCOTT BLAIR [1938] did not allow an elastic recovery and calculated the viscosity from the total strain under load. MOHR *et al.* [1948] determined a kind of yield-value and KRUISHEER *et al.* [1938] used a complex property involving both yield-value and viscosity. From this it is clear that one cannot compare the results of different methods without very careful consideration, since they are based on different principles and the dimensions of the data are not always the same. Nor should it be forgotten that it is not allowable to compare two sets of data, even when these are both given in terms of viscosity expressed in c.g.s. units, since they may have been obtained under different arbitrarily chosen conditions. Hence, the type of comparison made by DOLBY [1941] is not without risk. Dolby compared data from Scott Blair's parallel plate plastometer with his sectility (cutting) apparatus. He took the precaution of compressing and cutting at as nearly as possible the same velocity. Even so, the rate of deformation of the butter itself is by no means necessarily the same. The figures given by the two methods certainly show a relationship and this indicates, according to Dolby, that both methods determine the same consistency properties, so that the figures from one method can be converted easily into those derived from the other, but against this view it must be pointed out that Scott Blair determined a viscosity which was only meaningful under arbitrarily fixed conditions. Moreover, it is quite possible that a correlation may be found between data from different experiments, even when these measure quite different properties, e.g. viscosity and yield-value (see p. 120).

In attempting to compare different methods, it is useful to study the relationships between load, time and deformation. MULDER [1940] loaded cylindrical pieces of butter for 30 sec. with different weights and determined the total deformation. Under the conditions of these experiments, butter showed a yield-value. KRUISHEER & DEN HERDER [1938] loaded a penetrometer with different weights and determined the penetration after 30 sec. These authors also found a yield-value.

From a rheological point of view, there is no reason why butter need necessarily have a yield-value; indeed, as HOUWINK [1937] has pointed out, there is a sense in which no substance has a yield-value. From the practical point of view, however, it cannot be denied that under the conditions of Mulder's and Kruisheer's experiments, a yield-value does exist. Dolby's argument against it is not sound, since the presence of a yield-value is apparent, even from his own experiments. It is possible that he overlooked a constant when he calculated his logarithmic curves, and that since there is a connection between yield-value and viscosity (see p. 115), he failed to notice this constant factor at a later stage.

It must be emphasized that the magnitude of the yield-value which was observed is arbitrary. If conditions are changed, different values will be obtained; thus, according to MULDER [1947], the yield-value varies with the time of loading. According to the Dutch experiments mentioned above, it might be preferable to describe the behaviour of butter loaded only for a short time in terms of both yield-value and viscosity rather than of viscosity alone.

MULDER [1940] has studied the extent to which differences in consistency can be described in terms of viscosity and yield-value. He constructed deformation diagrams, using a series of different loads for 30 sec. over an area of 4 mm^2 on two sets of butter samples, one of which was prepared from cream cooled at a low temperature while the other was made from cream which had not been intensively cooled.

The two sets were studied immediately after working and also 6 hours and 6 days later. It is clear from Fig. 24 that the differences in consistency were very marked. Differences in firmness between the freshly worked and the set butter appear clearly in the figure. Although the butters were strikingly different in spreadability, they behaved in much the same way under load, the penetration curves being indistinguishable. From these experiments it follows that this method cannot demonstrate all types of consistency differences. Furthermore, it appeared that when yield-value increases, viscosity also increases.

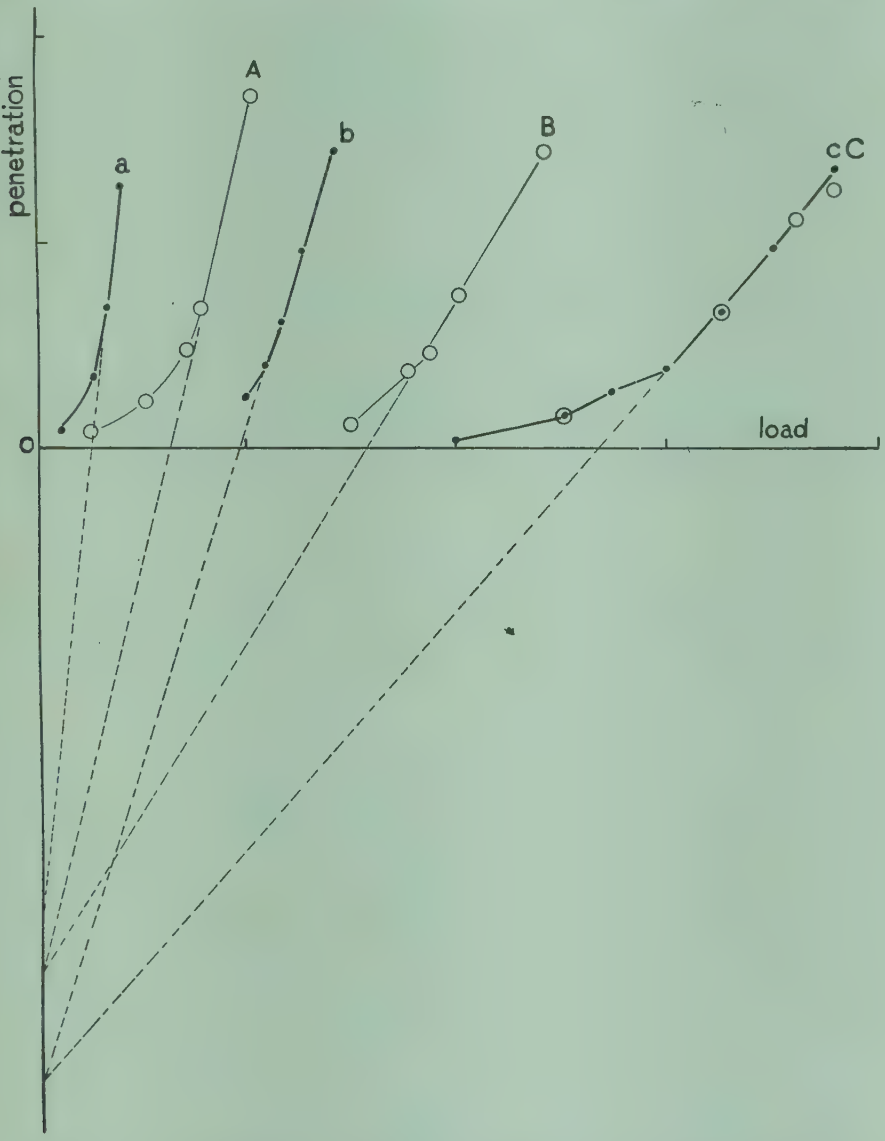

FIG. 24. Penetration Curves for Different Types of Butter.

There is a close correlation between these properties. The product of the theoretical yield-value and the cosine of the angle which indicates viscosity is constant. From this it follows that the straight portions of the penetration curves converge at a point, a conclusion which is in agreement with the data obtained by KRUISHEER & DEN HERDER [1938] from butter prepared in different dairies.

This relationship between yield-value and viscosity suggests that the distinction between these properties is more or less artificial, or at least, that both of them are in some similar way connected with the structural properties of the butter. It should not be forgotten that such yield-values and viscosities are arbitrary in character. In view of the

TABLE 13

Relationship between sectility, yield-value and viscosity

Method of manufacture		"Schnitt-festigkeit" cutting value (Sf)	Kegelfliess-punkt. yield-value K_f	Viscosity (η)	Sf/Kf	Sf/η	η/Kf
Alfa butter	1	91	0,68	11,4	134	7,9	16,8
	2	74	0,50	8,5	142	8,7	17,0
	3	27	0,19	2,63	142	10,3	13,9
	4	25	0,16	2,76	156	9,1	17,3
	5	17	0,111	1,88	153	9,0	16,9
	6	16	0,105	1,64	152	10,2	15,6
	7	156	0,81	15,6	193	10,0	19,3
	8	20	0,108	2,10	185	9,5	19,4
	9	18	0,083	1,53	217	11,8	18,4
	10	18	0,106	1,91	175	10,6	18,0
Fritz butter	11	45	0,33	9,0	136	5,0	27,3
	12	38	0,34	10,1	112	3,8	29,7
	13	12	0,045	1,10	267	10,9	24,5
	14	11	0,040	0,85	275	12,9	21,3
	15	10	0,041	0,99	244	10,1	24,1
	16	85	0,74	12,3	115	6,9	16,6
	17	42	0,39	8,3	108	5,1	21,0
	18	28	0,14	2,88	200	9,7	20,6
	19	20	0,09	2,04	222	9,8	22,6
	20	16	0,069	1,59	232	10,0	23,0
	21	16	0,066	1,18	243	13,6	17,9
	22	9	0,027	0,66	333	13,6	24,5

close relationship between them, it is probably not necessary to determine both yield-value and viscosity; only one of these properties need be measured or possibly a combination of the two such as is measured by the methods of Scott Blair and of Kruisheer and den Herder, and also when cutting and slicing tests are used. Moreover, the close connection between yield-value and viscosity, suggests a high correlation between various methods of measuring consistency, provided that the rates of deformation not do differ greatly.

Determinations with a small deformation may not be comparable with those for large deformations; for example, it is not permissible to draw conclusions about the capacity of butter to maintain its shape under the force of gravity from the results of measurements made with the penetrometer. Thus, Mohr and Schulz found no relationship between "Formfestigkeit" (rigidity of form) and "Schnittfestigkeit" (rigidity of cutting).

Mohr and his co-workers attempted to find relationships between a number of different methods in order to establish quantitatively a means of expressing the extent of certain defects in consistency, such

TABLE 14

Relationship between sectility, yield-value and sagging

No. of butter sample	S_F	K_f	S_f/K_f	Sagging
1	44,5	0,407	109	—
2	56,5	0,514	110	—
3	25,5	0,216	118	1,15
4	62,0	0,492	126	—
5	53,5	0,402	133	0,81
6	69,0	0,513	134	0,98
7	59	0,425	139	0,81
8	54	0,368	147	0,76
9	75	0,477	157	—
10	39	0,245	164	0,40
11	59	0,346	171	0,46
12	40	0,221	181	—
13	77	0,41	188	0,51
14	85	0,432	197	—
15	42	0,282	149	0,55

as brittleness. In Table 13 figures are given for sectility, cone yield-values and viscosity for butters of different kinds.

There seems to be at least an approximate relationship between the results of the different methods, but it is clear that the deviations are such as to make it impossible to replace one method arbitrarily by another. The causes of these deviations were not established. Table 14 gives data for sectility, cone yield-value and sagging properties.

According to Mohr and Schulz, there is no doubt that brittle butter sags less readily than does butter of good spreadability. When the butter is soft as a result of high temperature of the season of the year, the method is not applicable. A high air content is also disturbing. (For a comparison between spreadability and sectility, see Fig. 23 and for that between sagging and sectility, see Table 14).

2. 9. *Elastic Properties of Butter*

The elastic deformations in butter are not very large since this material does not show marked High-Elasticity.

Davis [1937] has described the elastic properties in terms of a modulus of elasticity which gives the relationship between the amount of elastic deformation and the applied force, but does not, of course, say anything about the maximum elastic deformation which can take place. According to Mulder [1947], it is unlikely that there are any important differences in elasticity between different butters. He concludes, therefore, that determination of elastic properties is not very important in assessing butter consistency.

Although the maximum elastic deformation is small, it does not follow that elastic properties have no importance at all. They give the butter a vivid appearance when spread, although the "dead" appearance of some butters probably cannot be attributed to a lack of elasticity, but is rather caused by a deficiency in flow properties (brittleness).

2. 10. *Conclusions*

In conclusion it may be stated that at the present time there are many different methods for determining the consistency of butter, but that no one of them is able to express consistency as it is judged by butter graders by the organoleptic method. One may well ask whether the methods of research which have been attempted in the past have not been too analytical in character. There is a parallelism between judging the consistency of such products as butter and judging the character of individual people. In the latter case also, analytical methods of approach have given rise to great difficulties and one should not look so much for single character traits, but should pay attention rather to the complex behaviour of the individual as a whole (the Gestalt approach). It is also possible that the use of factorial analysis as developed by Scott Blair will prove to be promising (see chap. VIII).

CHAPTER V

RHEOLOGY OF CHEESE AND CURD

BY

M. BARON AND G. W. SCOTT BLAIR
NATIONAL INSTITUTE FOR RESEARCH IN DAIRYING,
THE UNIVERSITY OF READING, ENGLAND

0. Introduction.

It is not always obvious to those unfamiliar with the dairy industry that rheological tests might play such an important part in controlling the processes of cheese-making or in expressing the quality of finished cheese. Indeed the industry itself has been very slow to appreciate the potentialities of objective rheological tests.

From the earliest times, however, the assessing of "body" of cheese and curd (partly made cheese) by subjective means has always been regarded as important. It has long been known that faults in body, especially at certain crucial stages in manufacture, have serious repercussions on the quality of the finished cheese; and that poor body in "green" (unripe) cheese foreshadows inferior keeping quality and even serious deterioration during ripening.

Now that cheese is appreciated to be the habitat of many varieties of micro-organisms, it is no surprise that the physical condition of this habitat plays a vital part in deciding the relative success of the competing organisms and, through them, largely controls those aspects of chemical constitution which are responsible for desirable and undesirable flavour and odour.

Unfortunately cheese and curd, in its various stages of development, have very complex rheological properties — probably more complex than those of most synthetic high polymers — nor is anything known about the molecular structures responsible for this complex behaviour. Thus, for example, the relative importance of entropy and energy high-elasticity has been compared for many polymers — though usually with considerable experimental difficulty — but, for cheese, such experiments would still prove insuperably difficult.

Rheological work has been, hitherto, of an essentially empirical kind and this situation is only likely to be improved when other physical methods, capable of elucidating something of the very complex molecular structures, have been applied to cheese.

Meanwhile, perhaps the most hopeful line of work, from the theoretical point of view, has been the still tentative application of statistical methods of multivariate analysis to correlation coefficients relating empirical tests. Even here, the statistical methods available are far from satisfactory. But a considerable amount of work has been done and this is, perhaps, not a bad time (1952) to review the situation. Readers who require a fuller account of this work are referred to a monograph which will be published by one of us almost simultaneously with the present book (BARON [1952]).

1. Early Work

The (British) National Institute for Research in Dairying has carried out a programme of research lasting for some ten years on the rheological changes which take place during the manufacture of hard-pressed cheese and on the relationship between rheological conditions during manufacture and the quality of the cheese in the store both as judged by experts (see Chap. VII) and as measured by instruments.

As DAVIS [1937] puts it:

> "So much importance is attached to the rheological properties of cheese that in England about 40 out of 100 marks awarded in grading are given for "body" and "texture". Although some authorities do not distinguish clearly between these terms it is preferable to define "body" as that quality which is perceptible to the touch; "texture" as that which is evident to the eye, excluding colour. Under the term "body" are included several factors, of which firmness (viscosity and modulus), springiness (elasticity) and smoothness (homogeneity) are most important. In grading, firmness is indicated as (1) very soft, (2) soft, (3) rather soft, (4) normal, (5) firm, or (6) over-firm, and smoothness as (1) silky, (2) chalky, or (3) gritty."

The ripening of cheese depends on the development of micro-flora and especially on the type of bacteria which preponderate and this, in turn, is controlled to a considerable extent, by the physical nature of their habitat.

Davis' experimental method consisted in the compression of cylinders of cheese under constant-load. Compressive stresses were not quite constant on account of the changing cross-section of the test-piece but the effect of this could not have been large in view of the comparatively small strains produced.

The cheese was considered in terms of complex models of Kelvin Bodies (coiled springs embedded in vaseline) and static friction units and the strains were divided into recoverable and non-recoverable components. The following typical properties are considered: (1) Elastic modulus, (2) Over-all viscosity (it is clearly pointed out that this is a mean viscosity during flow: viscosity is actually rising all the time if stress is constant), (3) Relaxation time which is related to springiness, (4) Internal viscosity which controls the rate of elastic after-effect, (5) Structural viscosity — i.e., ratio of viscosity at a low stress to that at a high stress, (6) Work-hardening, defined very generally to mean rate of increase of viscosity with increasing strain under constant stress, (7) True elastic hysteresis, by which is meant the ratio of shear moduli for conditions of rising and falling stress, and (8) Relaxation flow, i.e., internal flow during stress relaxation. Presumably (8) differs from (4) if, as is almost certainly the case, the Principle of Superposition does not hold. Crushing strengths are also measured.

Davis gives curves showing the replicability of tests on samples from the same cheese and, in a note added to the proofs, stresses the importance of remembering that there are moisture gradients in cheese so that replicate samples should be taken from the same depth in the cheese.

Curves are given for typical and prize examples of a number of sorts of British hard-pressed cheese — Cheddar, Cheshire, Leicester, Lancashire, etc., but the data were not treated statistically (it is doubtful if their number would have justified such treatment) and the work should be regarded rather as a pioneering attempt to show how rheological methods can be applied to different types of cheese than as giving accurate comparisons between the varieties.

Davis also describes some rather similar experiments on butter.

Similar to the work of Davis is that of MULDER [1945], of the Hoorn Experimental Station, Holland. Mulder compressed cylinders of cheese of height 1.5 cm and initial area 4 cm^2 between parallel plates, the deformations being magnified sixfold. No correction was made for the change in cross-section during loading. The strains were divided into recoverable and non-recoverable components from which viscosities ($\sim 1 - 10 \times 10^8$ poises) and compression moduli ($\sim 0.5 - 7 \times 10^6$ dyne/cm^2) were calculated. Edam and Gouda type cheese as well as curd (Wrongel) were studied. For long loading times ($\sim$ 10 min.) the total deformation and its elastic and plastic components are all approximately proportional to the applied load.

The pressure (g/cm^2) divided by the total strain produced in 10 sec. is taken as a measure of firmness ("Stugheid" lit. "Unyieldingness").

Using a simple dashpot-spring model, relaxation times are calculated and are found to be $\sim 800 - 3000$ sec.

Subjective assessments of elasticity were found to depend not so much on the relaxation time as on the immediate deformation.

Stresses needed to cause rupture were also measured and the ratio of these to compression moduli are given.

In a later paper MULDER & RADEMA [1948] describe methods for making Edam cheese at a low temperature (20° C) — often necessary during the second World War. Large quantities of calcium chloride and of hydrochloric acid were added to the milk.

2. Work on Curd

In the manufacture of almost all types of cheese, the milk is first brought to the required acidity and temperature and then converted into a gel by means of rennet. For making hard pressed cheese, the rennetted curd is generally cut into small pieces at a time when the gel has reached a suitable consistency. This consistency is partly defined by the nature of the surface in rupture (clean or flocculated) and partly by the resistance of the curd to compression. No adequate physical measurement of the former property is known, but the latter is best expressed by the shear modulus of the gel. SCOTT BLAIR [1938] has shown that for small displacements under loads applied for a few seconds, curd gels behave approximately as Hookean elastic solids and he describes an apparatus by means of which a light circular tray laid on the surface of the curd is loaded by means of an annular lead ring. In the middle of the tray is a small metal disk with which electric contact is made by lowering a pointed metal rod. The movement of the rod is recorded on a scale and indicates the displacement (ε) of the tray (radius r) under a compressive force F. The shear modulus can be calculated, assuming the vat containing the curd to be large in relation to the tray, from the formula:

$$G = F/8r\varepsilon \tag{1}$$

If measurements are repeated on the same surface of the gel, there is a tendency for G to fall due to some kind of elastic fatigue. Thus, if the process of "firming up" of the curd is to be followed, each reading should be taken at a different spot on the surface.

ROWLAND & SOULIDES [1942] have used a somewhat similar apparatus on a laboratory scale for studying the firmness of curd in beakers. It is suggested that this technique might prove useful as a pilot test to compare milks for cheese-making and the effects of addition of calcium chloride, changes in acidity, amount of rennet, etc. This test might fulfil the same function with regard to cheese-making as does the "curd-tension" method (see below) in relation to digestibility and suitability of milk for infant feeding.

The large scale apparatus has to be fastened to a special frame attached to the sides of the vat and takes a little time to set in position. The firmness of curd before cutting was later determined much more simply by means of a section of a hollow sphere made of plastic of standard weight and thickness which is lowered on to the surface of the curd by hand by means of a thread. Scales on the surface of the transparent plastic indicate the depth of indentation and check the evenness of sinking.

ALLEMANN & SCHMIDT [1916] were probably the first workers to measure the rigidity of rennetted curd by drawing a cutter through the coagulum and recording the resistance to cutting as the tension exerted on an attached spring. The cutter consisted of 3 concentric wire rings, 3, 5 & 7 cm diameter respectively, soldered together concentrically by means of a cross axis. The tests were carried out on 400 cc samples of milk rennetted under cheese-making conditions. With approximately equal coagulation times, the firmness differed for different samples of milk. HILL [1928, 1931] describes a similar instrument for measuring the curd tension of milk in terms of the pull in g. required to draw a 10 pronged star-shaped knife through 100 ml. of coagulated milk at 35° C., The instrument was modified to incorporate an automatic compression type of spring balance recorder and is manufactured under the trade name of "American Curd-o-meter" ¹) (The AMERICAN DAIRY SCIENCE ASSOCIATION [1941] recommends this type of apparatus for measurement of curd tension).

The curd tension of milk varied between and within breeds of cow. It increased when fat was removed but, surprisingly, most milk with high fat content, including goat's milk, was hard curded: boiling and evaporation both decreased the curd tension, and pasteurizing probably slightly decreased the value. The range of values for the samples taken, mainly from Guernsey and Ayrshire cows, was 15 to 200 g. Curd tension was higher in extremely cold weather.

HILL & MERRILL [1932] investigated the effect of hard and soft curd milks on the manufacture of cheese and found that the latter gave a higher yield. The fat loss in whey from soft curd milk was 30.3 % higher than from hard curd milk, and the cheese did not mat in the press. Again, the soft curd cheese ripened more quickly and tended to develop off-flavours.

LAUDER, MCGILLIVRAY & COMRIE [1934] describe a further modification of Hill's Curd-o-Meter in which the knife is drawn through the curd at constant speed and the force measured.

BURGWALD & ARMSTRONG [1937] found that increased speed of cutting lowered the curd tension number and that the surface of the coagulum was tougher than the interior. Curd tension increased slightly when the pH was raised slightly and also was higher for longer setting times.

A considerable amount of work bordering on rheology and concerned with the process the setting of milk into curd, is described in a recent book by KOPACZEWSKI [1950].

BERGGREN [1938a] modified the Bloom gelometer by replacing the plunger by a knife and obtained good agreement with Hill's apparatus for the measurement of curd tension. This former instrument was especially useful in determining low curd tensions. Investigating the effect of the addition of gelatine to milk, by Hill's method, BERGGREN [1938b] found that gelatine caused a fall in tension and that this value decreased when the viscosity of the gelatine was increased. Maximum curd tension occurred when the pH of milk before coagulation was 5. 8. The effects of homogenization and pasteurization on curd tension were investigated by KELLY [1941].

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¹) Manufactured by the Heusser Instrument Manufacturing Company of Salt Lake City.

MARCQUARDT & DENNISTON [1942] found that the curd strength of reconstituted evaporated milk was much less than that of commercial homogenized milk. STORRS [1941] showed that curd tension and curd surface area tests were independent factors showing no significant correlations. The relationships between catalase contents of milk and curd tension were studied by HASTINGS & EREKSON [1944].

ROGERS & SANDERS [1942] used a modification of the Curd-o-meter for measuring curd tension in the cheese vat. They also tested standard disks of cheese in an elastometer working on the principle of the Chopin extensimeter used for flour doughs. The samples were subjected to air pressure and the depth of the deformation served as an indication of the elasticity of the cheese. A measure of the plasticity of the cheese was found by placing a standard boring in a cylinder and subjecting it to increasing pressure till extrusion through an orifice occurred.

SPUR & WOLMAN [1942] curdled milk and then passed it through 3 sizes of sieves of decreasing mesh. The curd number was defined as 1a + 2b + 3c where a, b and c were the percentage number of particles retained by each sieve. The method, which was found to give results comparable to those of the Curd-o-meter, was useful in dealing with the coagulation properties of milk preparations as related to human digestion. SPUR [1948] investigated curd number and curd tension in relation to the digestibility by infants.

NORTH CAROLINA STATE COLLEGE OF AGRICULTURE [1946] reports the breed variation in curd tension of milk. Higher values occurred in spring than in summer, and Jersey and Guernsey breeds produced milk with a higher curd tension than did Ayrshire and Holstein (Friesian) breeds.

Several other methods for investigating the rennet coagulation properties of milk have been used. MATTICK & HALLETT [1929] studied the flow of milk and rennet through an orifice and SOMMER & MATSEN [1935] observed the formation of graininess of milk and rennet in agitated containers. Using a rotation viscometer, CHRISTEN & VIRASORO [1932, 1935] found that the viscosity of rennetted milk remained constant for a period after the addition of rennet and then increased and accentuated strongly towards the end.

KING & MELVILLE [1939, 1940] measured the viscosity of milk setting under rennet by means of an oscillation viscometer. The pendulum consisted of a cylinder, 2.54 cm diameter, 7.62 cm height and 300 g in weight. The surface was roughened to facilitate consistent results and an additional weight of 200 g was attached above the working cylinder. Coagulation time was defined as the time taken for the pendulum, with an initial displacement of 90°, to come to rest when 50 % of the standard quantity of rennet was added to the milk. The logarithmic decrement of sinking was used as a measure of the viscosity. HANSSON, SJÖSTRÖM & SAMUELSSON [1948] investigated the elastic properties of rennet curd by means of a "consistometer" [1]. This consists chiefly of a metal cylinder hanging from a stainless steel torsion wire. The wire is suspended from a revolving knob provided with a pointer and circular scale and the cylinder hangs in the centre of a thermostated metal container. Vertical grooves were made on the surface of the cylinder and the inside of the vessel to prevent gliding between the walls and the curd. The elasticity,

$$G = c.\ (\phi - \delta) \quad \text{where } \phi = \text{torsion angle of knob}$$

$$\delta = \quad ,, \quad ,, \quad ,, \ \text{cylinder}$$

c is a constant

δ was observed after 60 seconds, the temperature during testing being maintained at 30.5° C. There was a linear relationship between G and rennet concentration for concentrations up to 20 parts in 10.000. G was also related to the time after rennetting. Milk held overnight at 4° C showed a considerable decrease in its elasticity when rennetted. When the pH of milk was lowered with lactic acid, the elasticity increased in proportion. GOLDSMITH & IBALL [1949] describe a torsion device in which a small and decreasing stress is exerted on the visco-plastic substance by means of a blade attached to a torsion wire. The apparatus has been used to study the properties of milk curds. A modification of the Scott Blair–Nutting equation is suggested to account for the variation of both stress and strain with time and a "firmness intensity factor" of the substance is calculated by means of this equation from the observed relation between blade deflection and time.

MOLUSHKO [1950] a Russian worker, used a simple device for estimating the firmness of milk coagulum for Russian, Swiss and Dutch types of cheese. A hollow steel tube of fixed dimensions and weight was lowered into coagulated curd and the depth to which it

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1) Manufactured by "L.K.B.-Produkter", Fabriksaktiebolag, Sweden.

sank after 30 sec. was stated to give a measure of the firmness of the curd. No indication of the accuracy or correlation of this test with the quality of the curd is given.

Much work has been published on the chemical aspects of the causes of soft curd and slow-setting curd in milk but most of this falls outside the scope of this book. One paper, however, should perhaps be mentioned. CHEVALIER, MOCQUOT, ALAIS & BONNAT [1950] point out that there are really two distinct types of soft-curd milk: mastitis milk and milk which does not come from animals infected with any udder disease. These authors separated out the protein from a number of milks of the latter type as well as from controls; and, on reconstituting "milks" from them, were able to show that the characteristic strength or weakness of curd persisted, concluding therefore that the source of weakness in such milks lies in the protein.

An accurate knowledge of the firmness of the uncut curd is sometimes important for research purposes but is seldom of direct industrial importance. The next stage in the manufacture of hard cheese, known as the "scald", is in many cases the most important and crucial in the whole process. The curd, cut into small pieces, is stirred in the whey by hand or machine while the temperature is steadily raised. This process induces a syneresis in the individual curd particles which contract, expelling more and more liquid and increasing in firmness and resilience. In order to judge at what moment to terminate this heating process and to allow the curd to settle ("pitching", as it is sometimes called), the cheese-maker takes a handful of curd and, squeezing it hard with the fingers and thumb, judges its consistency. Reproducibility of judgment at this stage is vital if the quality of the cheese is to be maintained. Moreover the cheese-maker should know how to adjust the consistency at this stage to allow for abnormalities in acidity or to prepare a cheese having unusual keeping qualities.

No adequate method has yet been devised for measuring directly the rheological properties of curd at this stage, but it has been shown that the cheese-maker's requirements depend on the amount of whey which can drain out of the mass of wet curd. The required information can therefore be obtained by measuring either (1) the moisture content of the whole mass of curd (2) the density of individual pieces of curd, or (3) the superficial density of a mass containing both curd and trapped whey.

Since the exact timing of the process of pitching is quite crucial

— for some types of cheese such as Gruyère Comté one or two minutes may matter — method (1) would only be practicable if indirect methods, such as measurements of conductivity or dielectric constant, were used; and such methods are not well suited to such mixtures.

A number of workers have used method (2) — the main disadvantage being that the heterogeneity of the material generally necessitates a fair number of replicate tests. WINKLER [1930] was probably the first to measure the density of individual particles of curd by floating them in solutions of NaCl of known density. Later the method was developed by MÄDER [1936] for Emmental and Tilsit cheese and has also been used by CSISZÁR [1940]. This last author has related the consistency (subjectively assessed), moisture content and density of over 200 Hungarian Ovárer cheese (a type of Tilsit). He stresses the importance of taking samples of approximately uniform size by using a sieve sampler, since small particles tend to lose water more quickly than do larger particles and hence sink faster if the density is the same.

Method (3) has been developed by Scott Blair and his co-workers. SCOTT BLAIR & COPPEN [1940] describe the original test in which a cylindrical bucket made of standard mesh wire gauze is filled with a mass of curd taken directly from the vat and weighed. The curd is cast into a cylindrical testpiece which can be removed from the bucket and whose height can be measured. Since the diameter, but not the height, of this test-cylinder is controlled by the size of the sampling bucket, the superficial density is obtained by dividing the weight (W) by the height (h). Since whey continually drains from the sample, the timing of the processes required for the making, weighing and measuring of the test-cylinder was at first very carefully controlled until SCOTT BLAIR & SCOTT BLAIR [1941] later showed that such accurate timing was unnecessary, since the sample tends to lose weight (in the form of whey) and height at about the same rate so that the measured density does not vary very rapidly.

Scott Blair and Coppen (l.c.) found a high correlation ($r = 0.87$ on 197 samples) between W/h and moisture content of curd determined by the usual method. Data at moisture contents above 75 % were excluded from this calculation partly on account of lack of reliability and partly because the relation in this region of high moisture both ceases to be linear and is of no practical significance.

The curd was cut to three different sizes — abnormally coarse (for Cheddar cheese), medium, and abnormally fine. The size of cut did not affect the *W/h*-moisture relationship. During the process of scalding, the values of *W/h* were higher the coarser the cut, but the curves converged at the time when the curd had reached its normal pitching consistency.

The *W/h versus* time curves differed characteristically for different types of British hard-pressed cheese and to a lesser extent for the same type of cheese made in different factories.

In a later paper SCOTT BLAIR & COPPEN [1941] gave histograms showing the values of *W/h* for two factories making Cheddar cheese and compared the individual values with the cheese-maker's judgements as to whether the curd was soft, normal or firm when the test was carried out. The effects of temperature of scald, acidity, etc., were also studied.

Histograms were also given comparing a number of other British cheese: Caerphilly, Leicester, Double Gloucester, Derby and Cheshire. The last was made in three sizes and the mode value of *W/h* was found to increase progressively the smaller the cheese (The weights were approximately 27, 16 and 4 Kg).

It is found that quite wide differences in the mode value of *W/h* can be tolerated in different factories making the same type of cheese since it is possible to produce cheese of indistinguishable quality by somewhat different processes. But it was also found that good quality cheese-making is invariably associated with a small scatter in the day-to-day and vat-to-vat variations in *W/h*.

In relating the values of *W/h* to the quality of the finished cheese, rheological tests on the latter were made as well as experts' subjective assessments. A ball hardness tester is described which measures the size of indent of a sphere pressed into the surface of the cheese under fixed loading and time conditions, as well as the proportion of elastic recovery after the load is removed. A skewer of the standard type generally used by British cheese judges was fitted with a spring handle and the force required to drive this into the cheese at a steady rate was recorded.

DAVIS & SCOTT BLAIR [1940] discuss the relationships between a number of chemical and rheological factors and propose graphical methods for making factory records. A specimen diagram is shown in Fig. 1.

SCOTT BLAIR, COPPEN & DEARDEN [1941] have studied "the effects of varying pitching consistency and rate of scald on the physical and

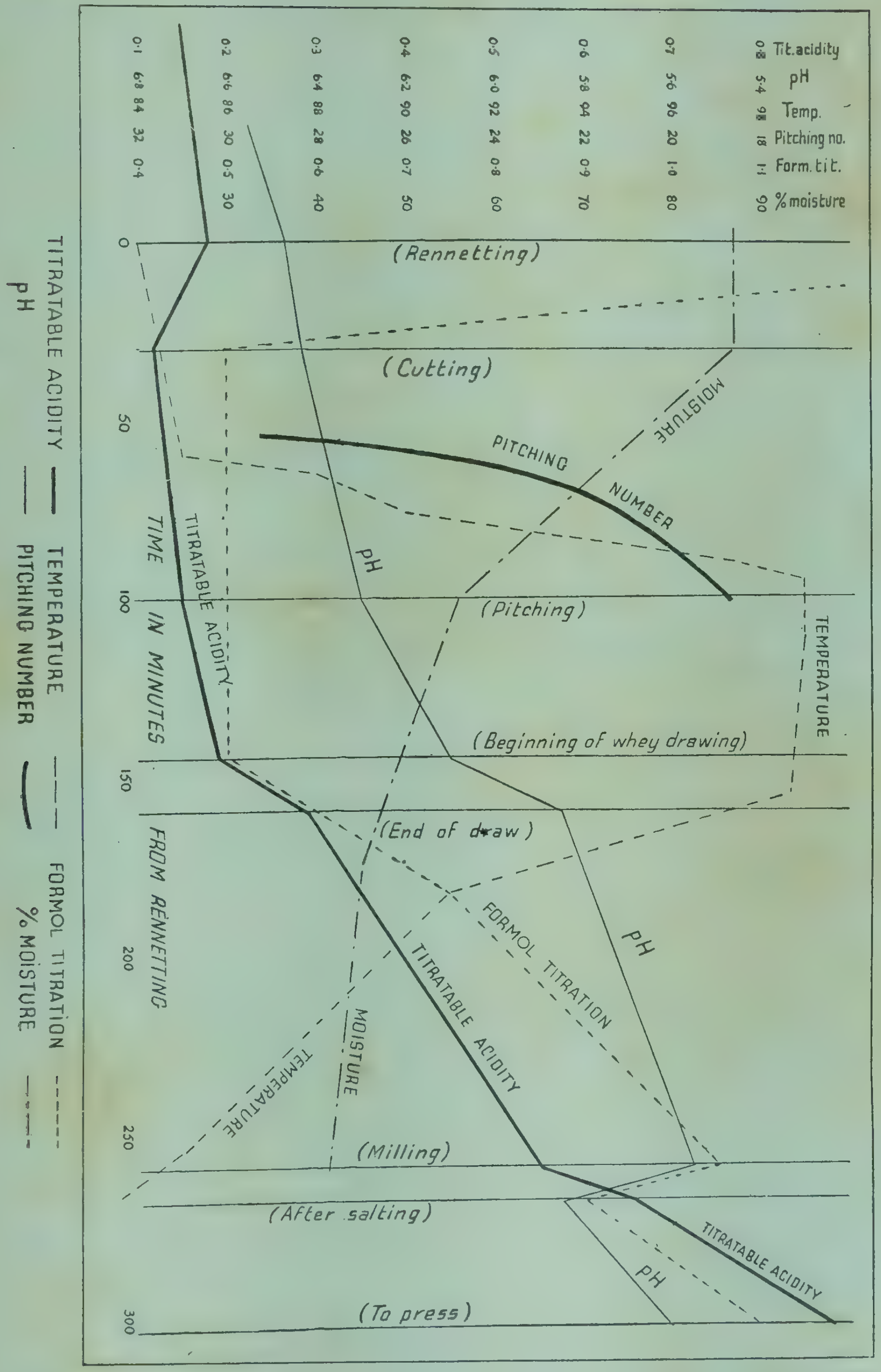

FIG. 1. From Davis and Scott Blair. Dairy Industries 5, 309 [1940]. Paper 65. Fig. 3. J.G.D. & Dairy Industries

chemical properties of Cheddar cheese and on the firmness of the cheese as judged by cheese-makers, bakers and others." (The psycho-physical aspects of this work will be dealt with in Chap. VIII.)

Six cheese were made under conditions as similar as possible, except that the W/h value at pitching and the rate at which the temperature was raised, were varied. Chemical and rheological analyses, moisture contents and vapour pressures were compared with the judgments of skilled cheese-makers, bakers who are skilled in a somewhat similar but essentially distinct technique, and non-experts.

The results were somewhat complex but strongly supported the hypothesis that the consistency of curd at pitching and the rate of scald are of the greatest importance in defining cheese quality and that the W/h measurement gives a reliable and effective measure of the former factor.

In a contribution to a Symposium on Cheese held at a joint meeting of the Food Group of the Society of Chemical Industry and the Society of Public Analysts, SCOTT BLAIR [1941a] proposed that for specifying the rheological behaviour of cheese, it might be advantageous to relate strain and time in constant stress experiments by means of a power law rather than to divide the strains into viscous and elastic components. Hard pressed cheese appears to give good linear relations between logarithmic strain and logarithmic time and, for a series of constant stresses, the strain after any given time is very closely proportional to stress. Any single cheese sample can thus be described not by a complex series of viscosities and elastic moduli, but by two constants only, the slope (k) and position (ψ) of the power-law curve. At this stage, this treatment was entirely empirical.

In a later paper, SCOTT BLAIR, COPPEN & DEARDEN [1942] have gone on to study the effects of pasteurization of milk on rheological and other conditions in the making of Cheddar cheese and also of quite large differences in the acidity of the milk.

With the exception of vapour pressure and "springiness", the effects of varying W/h were much more marked than were those of rate of temperature increase in the scalding process. Many physical properties measured during the ripening of the cheese, were correlated with W/h, but the rates at which these properties changed during the ripening process did not correlate well. Over-pasteurized milk gave a rapid increase in consistency (fall in W/h)with time but the curd did not become as firm as that from normal milk by the end of

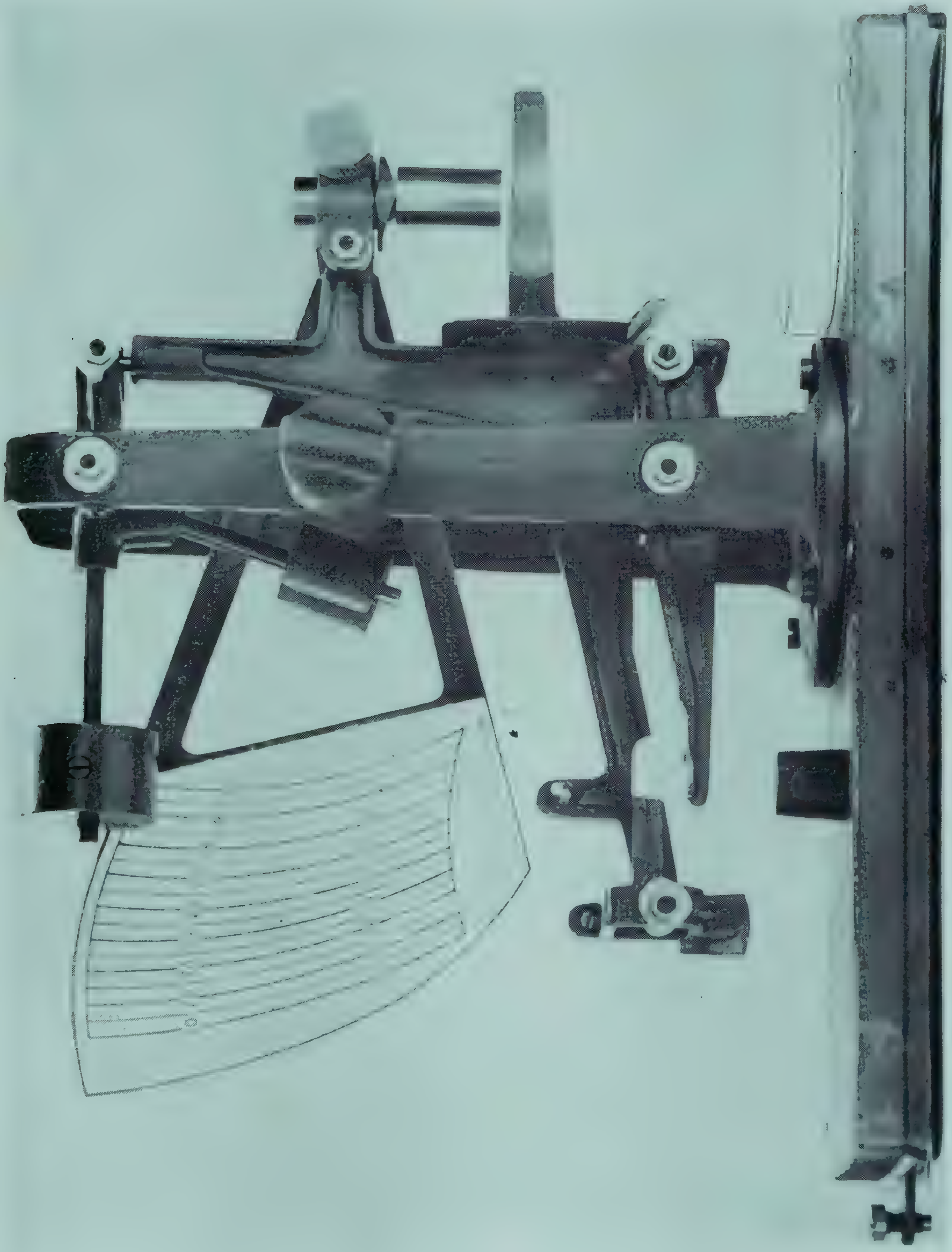

FIG. 2

Copyright "The Dairyman" and Mr. J. E. Caffyn.

the scalding process. Even lightly pasteurized milk showed a similar trend. But in general, consistency may be said to have been improved by light pasteurization but damaged by over-heating of the milk.

3. Finished Cheese

Approximately contemporary with the work of Scott Blair and his co-workers (though starting somewhat earlier) is that of Koestler in Switzerland (KOESTLER [1931; 1938; 1940a, b, c, d, e, f, g, h; 1941a, b; 1942a, b, c; 1943; 1946a, b, c; 1947a, b, c]) on Emmental cheese.

Koestler considers cheese and cheese curd as gels and much of his work is concerned with colloid chemistry rather than with rheology. Of interest to rheologists are his methods for loading cheese under compression and tension and his work on toughness ("Zerreissbarkeit"). The parameters which he derives from these tests are considered in relation to the colloidal conditions, the Hofmeister series of ions, etc.

For the compression experiments, very small blocks of cheese (6.5 × 6.5 × 25 mm) are loaded over a period of 2 min. after which the load is removed and, two min. later, the amount of both total and recoverable deformation is recorded. The reader is warned that in one of the papers [1940] there is a misprint in the definition of the percentage elasticity which is given as 100 $(l_1 - l_2)/l_1$ where l_1 is the total deformation and l_2 is wrongly quoted as the recoverable deformation ("Deformationsrückgang"). l_2 should, of course, be the non-recoverable part of the deformation, and is correctly so defined ("Einkürzungsrest") in the earlier paper [1931]. The writers are indebted to Professor Koestler for his courteous help in clarifying this point.

As well as the terminal figures for elastic and plastic deformations, complete loading and recovery curves are given with readings taken every 15 sec.

For experiments in tension, strips of cheese, some 9—10 cm long and of cross-section 5 × 5 mm are extended under constant load. Not only the elastic and plastic regions can be studied in this way but tensile strength and ductility can also be measured. The ductility („Bruchfestigkeit" — but it will be seen that this is the correct translation in view of the definition) is given by the increase in length of the specimen at rupture divided by the unstrained length. As an example of the values obtained for this ratio, tests on 11 cheese are quoted with an average value of 0.082.

The most interesting paper from the purely rheological point of view is [1940a] in which the influence of various factors on the rheological parameters and particularly on the percentage elastic recovery ("elasticity") is discussed. The elasticity increases somewhat with increasing temperature (approx. range 14 — 19° C) and pressure, except that in the case of cheese of weak body, there would seem to be an optimum pressure. Increasing salt content decreases the total deformation but does not regularly affect the elasticity. Moisture content variations (within limits) do not affect the elasticity nor, surprisingly, does age between 7 — 11 months. Variations in the elastic properties in different parts of the same cheese are not simply correlated to measurable chemical differences.

In another paper [1940c] the essential rheological properties of curd are described in terms of two bipolar qualities: hardness-softness and structured-unstructured ("fein-zäh"). Hence there are four distinct extreme types of curd: hard, structured; soft, structured; hard, structureless; soft, structureless. The resistance of the curd to penetration gives an important indication of these conditions, and in a later paper [1943] both the total and elastic deformations are shown to diminish on ageing.

In continuing the work on the rheological properties of British cheese, most of the experiments were carried out in commercial factories making either Cheshire or Cheddar, as it was desirable to test large numbers of samples and to treat the results by statistical methods.

Caffyn [1945] tested the rheological properties of Cheshire cheese from 20 different vats made on separate days, both during manufacture and during ripening in the store. Besides using the apparatus described by Scott Blair & Coppen [1940] for measuring the superficial density of the curd at pitching, he also measured the rheological properties of the curd during the Cheddaring process, i.e., after the whey has been drained from the vat and the curd blocked and turned to allow as much free whey as possible to escape, and the acidity to develop sufficiently. Before milling, the cheese-maker assesses firmness, toughness and springiness by pressing with his fist and tearing the curd apart. The "sectility" of the curd at this stage, and later of the finished cheese, was measured by means of a sectilometer consisting essentially of a taut wire, which acts as a cutter and is attached by means of a vertical rod to a container into which lead shot falls at a steady rate. The time to cut through two standard blocks, each

54 × 29 mm, is taken as a measure of the sectility of the curd. In general, there was a trend for this figure to increase during cheddaring but variations were introduced due to the turning of the curd and the position of particular blocks of curd under test.

A constant stress rheometer (see SCOTT BLAIR [1941b]) was also used for curd and cheese which recorded changes in the height of a cylinder with time. (A mechanism of bent levers increases the load so as to compensate for the increase in cross sectional area). A slightly modified version of the ball hardness tester was used to measure properties of the finished cheese. Three readings were obtained on any sample: (1) the total deformation after 5 seconds, (2) the amount of recovery in the next 5 seconds and (3) by difference, the plastic deformation, remaining after this time. The advantage of this "ball compressor" is that it does not require destructive sampling of the cheese.

The results showed that (W/h) was influenced by the solids-not-fat (S.N.F.) content of the incoming milk, high S.N.F. resulting in a softer curd. W/h was also related to log ψ from the constant stress rheometer at milling and to the % plastic deformation of the "green" (unripe) cheese.

The sectility of the curd at milling appears to be related to the ball compressor readings on the green cheese, though this measure is not satisfactory, due to the variation in sampling, already mentioned. Relationships between the rheological properties of the curd and of the green cheese did not persist during ripening and it was concluded that during this time variabilities are introduced which are independent of previous treatment. Wide differences in the rheological measurements taken at the top and bottom of the cheese were found, probably due to the uneven distribution of moisture.

CAFFYN [1946] later controlled the manufacture of one vat each day, by keeping to a strict time and temperature schedule, and standardizing mechanical operations. He varied the pitching number, the titratable acidity at milling, and consequently the cheddaring period, and the pressure at pressing, using 3 standards for each. Thus, in all, 27 different types of cheese were made. The finished cheese were tested instrumentally using the ball compressor, sectilometer and constant stress rheometer and were also graded for firmness and quality by an experienced grader. Total and partial correlations between all the measurements were calculated and from these, the following conclusions were drawn. The solid-not-fat content (S.N.F.) of milk influences the firmness (measured with the ball compressor) and moisture content of green cheese, as does the firmness at pitching. Very little relationship seemed to exist between the acidity at milling and the properties of the cheese, but the time to acquire this acidity influences the moisture content and possibly the firmness of the green cheese. As would be expected, the firmness is related to the moisture content but not to the fat content of the cheese. And apparently the pressure at pressing, which was varied from 20 to 60 lb./in.^{2} (1.4 to 4.2 Kg/cm^2) had no effect upon the rheological properties (In New Zealand WHITEHEAD & JONES [1946] found that hydraulic pressing almost eliminated mechanical openness in normal cheese of good quality and was thus superior to hand pressing).

From all the cheese made under these standard conditions 30 were selected and re-tested when between 2 and 4 months old. In placing these in order of firmness, the grader was in almost complete agreement with the ball compressor measurements. Only when cheese had abnormal elasticity was there any discrepancy, the grader upgrading for firmness highly elastic cheese and *vice versa*. However, no evidence was forthcoming to show that the particular type of body could be predicted by external instrumental tests. The ball compressor tests, moisture, sectility and dissipation coefficient were interrelated. High moisture content is associated with inferior firmness and low elasticity, low sectility and high k.

The author found little relationship between the rheological properties of the green cheese and of the ripened product but this is probably due to the fact that the conditions of storing were uncontrolled. Very few factory stores do have adequate temperature and humidity control even though this is of vital importance to the quality of the ripe cheese.

Since Caffyn carried out his experiments some of the apparatus used for measuring rheological properties has been improved and new instruments introduced. CAFFYN & BARON [1947] describe some of this equipment which includes the plastic bowl for measuring the firmness of rennetted curd and, mentioned above, new designs of the pitching machine and ball hardness tester ¹), a smaller "ball compressor" for measuring corresponding properties of cheese curd, and a

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¹) Patents held by Kraft Foods Ltd.,

mechanical borer. The advantage of the new pitching machine (Fig. 2) is that it now measures the weight and height of the curd sample simultaneously and the ratio W/h can be read off the attached scale.

The ball compressor is loaded by means of a standard weight which acts on the sphere by means of a series of levers, instead of the force being applied by hand, as previously, and the borer is a simple device for measuring the penetrability of cheese. It consists of an ordinary cork borer, 2 cm in diameter which is attached by a vertical rod to a loaded plate. The rate and depth of penetration is read off the attached scale.

A modification of the ball hardness tester is described by SCOTT BLAIR & BARON [1947] in which the constant load is replaced by a beam along which a weight is drawn at a steady rate, thus increasing the load on the indenting sphere. The rate of increase in load can be arranged to compensate for the increase in area of contact between the sphere and the material so that a constant stress is obtained once the initial accelerations have died down. For cheese, $\log \Delta = a + b \log t$ when the stress is constant, where Δ is the deformation at time t after the application of the initial load, and a and b are constants. This instrument has been called provisionally a "Meyer Hardness Tester".

These instruments were used by BARON [1947] in both Cheddar and Cheshire cheese factories. Graphs are given to show how rennetted curd increases in firmness as measured with the plastic bowl before it is cut. Working on similar lines to CAFFYN [1946] she confirmed his results as to the relationships between firmness at pitching and properties of the finished cheese and also found that the acidity at milling was correlated with the firmness of the cheese measured with the ball compressor and the penetrability measured with the borer, — the higher the acidity, the firmer and less penetrable the resulting cheese. Contrary to Caffyn's findings, no relationship between Cheddaring period and rheological properties was evident. The firmness of the curd at rennetting appeared to have no effect on the future properties of cheese. The difference between correlations involving the ball compressor and those involving the borer indicate that these two instruments are measuring different properties of the cheese, the first being more concerned with external and the second with the internal variations.

Experiments involving complete control of the making of Cheddar cheese with standard variations in rennetted curd firmness, measured by the plastic bowl, curd firmness at pitch measured by the pitching machine and acidity at milling, were carried out by BARON [1949a, b]. The resulting cheese were tested in the store at regular intervals throughout the ripening period and it was found that the firmness increased with age, rapidly at first and then more slowly, and that the relationship between firmness and pitching number persisted throughout. The "springiness" (elasticity) of the cheese decreased with age and it appeared that there was an optimum value of firmness at pitch for producing normal elasticity. Either side of this value, this factor was decreased.

Expert judgements were made on 5½ months old cheese for body and flavour. The firmness judgements were again in complete agreement with the ball compressor measurements and 100 % of the cheese pitched firm were judged to have satisfactory flavour, compared with 88 % of those with a normal pitching number and only 60 % of those pitched soft.

Several cheese were cut up and tested internally with the ball compressor and borer. Very little variation was found, though the centre of the cheese tended to be somewhat softer than the outer edges. This lack of variation was due to the regular turning of the cheese in the store.

Correlation coefficients showed that the relationships between the manufacturing process and the properties of the cheese were most clearly seen 14 days after manufacture, and in most cases the influences persist during the ripening. The firmness of the curd before cutting was found to influence the elasticity of the cheese — soft cut giving rise to high elasticity, and the firmer the curd at pitch, the firmer was the resulting cheese. The acidity of the curd at milling, and to the same extent its pH, were also related to the elasticity — high acidity corresponding to a soft plastic product.

The statistical technique known as Factor Analysis (see Chap. VIII) and hitherto mainly used in the field of psychology, was applied to some of the rheological measurements made on cheese during the latter experiment, by HARPER & BARON [1948]. Correlation matrices for 6 tests on 250 Cheddars were analysed by Thurstone's Simplified Centroid Method (THURSTONE [1933]). Three factors, or independent sources of variation, were obtained, which, from an analysis of the loadings, were suggested to be related to "hardness", "springiness" and "hardening" respectively. The borer and ball compressor tests were both highly saturated with the first factor. From this initial calculation, the authors claim that Factor Analysis shows promise of giving valuable information where mechanical properties of complex materials are to be compared.

To investigate the efficiency of Factor Analysis as a statistical method applicable to this type of physical testing a battery of mechanical tests on Cheshire cheese in the store was carried out by BARON & HARPER [1950]. Six instruments were used from each of which two or more separate but partially dependent measurements could be obtained. These instruments included the ball compressor, the "Meyer hardness" tester, and the borer, all of which have been described previously, and also a needle penetrometer, based on the principle of the standard penetrometer for bitumen testing, a spring skewer by which the resistance to penetration of a standard grader's skewer could be measured and a pendulum type of breaker, similar to the Izod tester, for measuring the energy lost in breaking a boring of cheese. It was hoped that the latter test would give a measure of crumbliness.

Besides these tests, assessments of some rheological properties of the cheese, such as firmness, springiness, etc., as well as of overall quality, were made by a panel of subjects.

Multiple Factor Analysis was applied to the data and the method of calculation and construction of three-dimensional models to illustrate the various relationships are described.

The results of the analysis have led the authors to the following conclusions, some tentative, others more definite.

Four factors are required to account for the observed correlations between tests. There is no suggestion that the subjective ratings give information which is apprecially different from that derived from the instrumental tests.

The instrumental test correlating most highly with the assessment of quality is the needle penetrometer carried out after the rind is removed while this same test *through* the rind is most similar in qualitative composition to "springiness" assessed subjectively by thumbing.

There is a systematic difference betweeen tests carried out through the rind and those carried out after removal of the rind.

The ball indentation tests and the penetration tests fall into two separate groups.

A similar programme was carried out in the same creamery in the following year. Some new tests were introduced and the pattern of relationships obtained in the two separate studies was very similar (Harper & Baron [1951]).

Further experiments, as yet unpublished, seem to indicate that the properties of Cheddar cheese vary considerably from those of Cheshire.

Eleven of the same Cheshire cheese were examined in detail by means of rheological and subjective testing during a two months ripening period in a well controlled commercial store by Baron [1949c]. Variations in the curves plotting mechanical properties against age of cheese show distinct differences between cheese of good and bad quality and can be used to predict to some extent their future quality.

Hadland [1951] in Sweden, has used the ball compressor, which he calls a "John Bull Indicator" for measuring the consistency of a typical Scandinavian whey cheese, "Mysöst". Briefly, he found that the plastic deformation was directly proportional to the total deformation. As with English cheese, the degree of elasticity decreased with the firmness. There was a correlation between this instrumental measure of firmness and the solid content, and an inter-relationship between these two properties and the grading score. "Consistency" scores and total solid content both tended to increase with increasing firmness. The author found the instrumental measurements consistent and useful in grading cheese some time before it was ready for sale and he gives limits within which the ball compressor readings must lie, if the cheese is to attain high grading scores.

In the U.S.S.R., Belousov [1949] has studied the crumb structure of cheese as the crumbs are distorted by the processes of manufacture and storage. The crumb size is also shown to vary systematically in relation to the distance from the centre and rind of the cheese. Various types of cheese, Soviet, Dutch and others, are studied: some makes are cylindrical, some are rectangular. The distribution and mean size of the holes ($\sim 10\ \mu$) within different layers of cheese are also discussed.

Kazantsev [1950], another Russian worker, devised an apparatus for measuring the elasticity and consistency of cheese curd. Curd of Altaĭ cheese was compressed by means of a flat plate within a wire gauze container. The forces required to produce elastic displacements, and also to press the curd through the gauze, were measured. Then the mass of curd was broken in two, by opening the container which was in two parts, hinged at the bottom, and the force required for this operation was measured.

Davidov & Barabanshchikov [1950], used a Höppler consistometer to measure the overall consistency, elasticity and viscosity of Dutch cheese. They studied the effects of pasteurization and found that these could be counterbalanced by the addition of about 0.05 % calcium chloride.

Saxl [1938] describes a modified Bloom penetrometer which can be used in cheese testing.

Roundy & Price [1941] have used a penetrometer for measuring the body of cream cheese. The plungers were made with cones of diameters 4, 8 and 10 mm, their heights being 1½ times the diameters. The resistance offered by the cheese when the plunger is forced into the surface is measured in grams. Sommer & Matsen [1935] had previously described this type of measurement.

King [1950] reviewed the properties of, and various tests carried out on, cheese and other milk products, but there is very little of rheological interest in this article.

In co-operation with the (British) National Institute for Research in Dairying, work has been carried out on the rheological properties of Gruyère (Comté) cheese at the Station Régionale de Recherches Laitières, at Poligny, Jura, (France).

Mocquot, Scott Blair & Baron [1947], and Mocquot, Scott Blair, Baron & Jeandot [1948], have measured W/h in the scalding process in the manufacture of Gruyère cheese, for which much higher temperatures and finer cuts are used than are needed for the English Cheddar variety. In the case of all English varieties, W/h had been found to be invariant to variations in W, thus the exact size of samples collected from the vat was found to be immaterial to the result of the test, within quite wide limits. For Gruyère curd, however, there were persistent slight variations and it was established that the invariant ratio was $W^{0.8}/h$.

Somewhat later, Mocquot found (private communication) that this effect was due to an artifact, the test-pieces being somewhat deformed in shape unless a different mesh of wire is used for the sampling bucket. When the mesh of the bucket is chosen appropriate to the altered size of cut, truly cylindrical samples are obtained and the use of the exponent 0.8 is eliminated. The following results were obtained:

(1) The higher the fat content of the milk, the softer the consistency at pitching, other things being equal.

(2) The effect of size of particle on values of W/h seems to be the

opposite of that found for English Cheddar. It would appear that there is a minimum value for W/h for a certain size of particle and that Cheddar lies on one side, and Gruyère normally on the other side of this minimum.

(3) Correlation coefficients between W/h and moisture content were not nearly as high as in the case of Cheddar.

A study was also made of the rheological properties of the cheese during the process of ripening. The sphere hardness tester designed by Scott Blair and his co-workers (see above) was found to be most suitable for assessing the "body" of Gruyère cheese and especially as a means for predicting the potentialities of the cheese for ripening while still at an early age.

Gruyère cheese, as is well known, develops spherical holes or *yeux* as a result of the production mainly of hydrogen gas by propionic bacteria. Such action is prevented in Cheddar cheese by the early addition of salt during the manufacture.

Gruyère cheese also sometimes shows long narrow cracks (*lainures*) which appear to be quite independent of the *yeux*. The formation of *lainures* is related to the hardness of the cheese as measured by the sphere hardness tester.

The effects of varying quantities of salt on hardness are also discussed.

The fact that tolerably good Gruyère cheese often contain some *lainures* is interesting, especially since these cracks tend to lie at very characteristic angles at different depths within the cheese. This suggests systems of undissipated stresses within the cheese itself, caused, no doubt, by shrinking and swelling as a result of moisture and temperature changes. But the *yeux* should be, and often are quite spherical and appear to be independent of the systems of *lainures*. The implications of these interesting engineering problems are briefly discussed by REINER, SCOTT BLAIR & MOCQUOT [1949].

Fig. 3 shows a cheese containing *lainures* and clearly illustrates the characteristic angles at which they lie.

SCHWARZ & FISCHER [1943a, b] have loaded cylinders of cheese and calculated compression moduli from recoverable deformations. A cone hardness tester is also used. But the principal work of these authors has been done with a Höppler consistometer in which a ball is forced, under pressure, through the material. This method is used for cheese differing as widely as do Tilsit, Edam, Camembert and Parmesan.

In this way, flow curves (stress *vs* rate of shear) can be plotted. The effect of varying temperature on such curves is also measured.

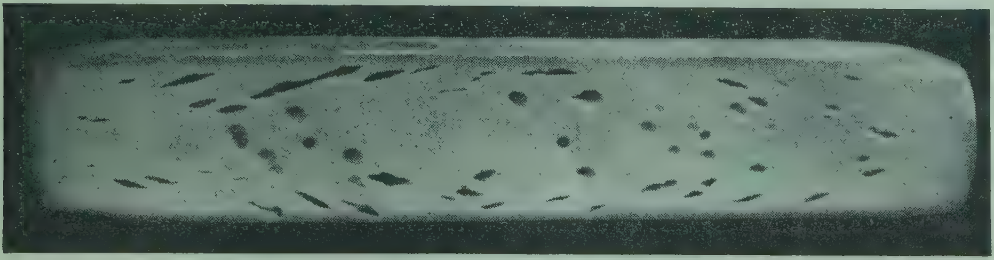

Fig. 3. From "Le Lait" Reiner, Scott Blair and Mocquot,

The flow curves are in general of the Bingham type, i.e., linear but making an intercept, on extrapolation to the stress axis. As a means of characterizing individual cheese, the stress required to produce a flow rate of 10^{-3} cm/sec. was selected. Thixotropy is characterized by the expression $(\eta_\omega - \eta_a)/\eta_a$ where η_ω is the "viscosity" of cheese or curd in the rested (gel) form and η_a is that of the worked material. The influence of ripening on these empirical rheological constants is also discussed.

Templeton & Sommer [1930] examined the "body" of processed cheese by measuring the force required to crush 1″ (2.5 cm) cubes of the material to half their original height. In the apparatus they used, which had a mechanical advantage of 5 (efficiency not stated), a crushing force of 800 — 1200 g indicated a cheese of good body.

CHAPTER VI

THE RHEOLOGY OF HONEY

BY

J. PRYCE–JONES
HORNSEA, ENGLAND

0. Introduction.

Honey may be defined as the concentrated solution of sugars prepared by bees from the nectar of plants. The definition includes nectar obtained from both floral and extra-floral nectaries but it does not include honeydew. Honeydew is not secreted by plants but it is obtained from leaf-sucking insects, especially aphids. These insects feed on the sap of plants; they extract its protein content, by means of a delicate filter in their digestive organs, and secrete the remainder as a clear sugar solution which spreads over the leaves and twigs. The bees collect this sugar solution and treat it in the same way as they treat nectar. As honeydew is often found in honey it is advisable to enlarge the above definition and describe honey as the concentrated solution of sugars prepared by bees from the sweet juices of plants.

In its simplest form nectar is a solution of sugar in water, but the nectar of a great many plants contains dextrose and laevulose. The sugar content of nectar varies from 5 % to 75 % but bees do not normally gather nectar of less than 15 % sugar content. Nectar is collected from flowers and transferred to the honeycombs in the hive, at some stage in the transition the bee adds a trace of the enzyme invertase which resolves the sucrose into dextrose and laevulose. At the temperature of the hive, water is evaporated until the honey contains at least 80 % sugar. The process of converting nectar into honey is known as "ripening". If the concentration of sucrose in the parent nectar is 20 % and the concentration of sugars in the ripened honey is 80 % the conversion may be expressed as:

NECTAR		$\xrightarrow{\text{Invertase}}$	HONEY	
sucrose	20 %		dextrose . . .	40 %
water	80 %		laevulose . . .	40 %
			water	20 %

Honey as obtained from the hive bears very little resemblance to the ideal honey shown by this conversion. The product from the hive differs in two most important respects, namely the dextrose/laevulose ratio is hardly ever equal to unity, and it contains a great many components besides dextrose and laevulose. The infinite variety of honey, derived from a large number of floral sources grown under widely different conditions of soil and climate, arises from the differences in the parent nectars. Apart from sugars, nectar may contain proteins, dextrins, organic acids, essential oils, dextrans, enzymes, traces of vitamins, tannins, minerals, pollen grains and yeasts. All these components will therefore be present in a more concentrated form in the ripened honey. The analyses of honeys indicate that, in general, they contain 2 % or more of unchanged sucrose and 5 % or more of "Undetermined Content". The famous paper by BROWNE [1908] still remains the classical reference on the composition of honeys, but more recently THOMSON [1936] made an extensive study of New Zealand honeys, ECKERT & ALLINGER [1939] of Californian honeys and VON FELLENBERG [1946] of Swiss honeys.

These various papers give complete analyses of a large number of honeys (apart from their "Undetermined Content" which is one of the most important factors in determining the viscosity of honey); but it is sufficient for our purpose to limit our attention to those components which can be directly correlated with the rheological properties of various honeys, as illustrated by the examples in Table I.

The practical beekeeper and purchaser of honey makes a rough estimate of the viscosity (which he describes as "body") by observing the rate of ascent of a bubble of air through the honey after inverting the container. This estimate of viscosity is assumed to be a measure of the degree of ripening of the honey, in other words a measure of its sugar content. It is a very unreliable guide, as the viscosity of honey depends not only on its sugar content: it is very sensitive to slight variations of temperature and still more to the presence of even small amounts of impurities such as proteins. The viscosity of honey is a very important factor which influences its rate of extraction from the combs, the amount which adheres to the combs, the facility with which it can be poured into containers, the rate of straining, clarification from air bubbles, ease of spreading and its hygroscopic properties.

TABLE I

The variable composition of honeys

Component	A	B	C	D	E	F	G
	%	%	%	%	%	%	%
Water	10.2	17.4	18.4	16.6	21.2	18.2	19.3
Laevulose (L)	44.6	35.7	47.0	39.7	38.0	36.2	31.3
Dextrose (D)	39.8	40.1	24.2	38.4	35.7	35.6	24.6
Sucrose	1.8	3.2	4.6	1.9	1.2	1.2	2.2
Melezitose							8.7
Dextrin					0.2	0.1	11.3
Protein					1.8	0.2	0.3
Dextran						5.3	
"Undetermined"	3.6	3.4	5.8	3.4	1.9	3.2	2.3
L/D Ratio	1.12	0.88	1.95	1.03	1.06	1.02	1.27

A. A sample of cotton honey (*Gossypium sp.*) from South Carolina.
B. A sample of blue curls honey (*Trichostema lanceolatum*) from California.
C. A sample of tupelo honey (*Nyssa aquatica*) from Florida.
D. A sample of clover honey (*Trifolium sp.*) from New Zealand.
E. A sample of heather honey (*Culluna vulgaris*) from Dartmoor, England.
F. A sample of *Eucalyptus ficifolia* from Stellenbosch, Union of S. Africa.
G. A sample of honeydew honey from Switzerland.

THE VISCOSITY OF HONEY

As indicated in the above table, honeys differ widely in composition and it is therefore not surprising that they display a wide range of rheological properties. In general honeys are Newtonian liquids but heather (*Calluna vulgaris*) honey — which is one of the most important European honeys — is thixotropic and various honeys derived from *Eucalypti* are dilatant. Not only are these properties of great rheological interest but they also have a great influence upon the methods of extraction and the general properties of the honey. It will therefore simplify the method of treatment of their rheological properties to classify honeys into (1) Newtonian honeys, (2) thixotropic honeys and (3) dilatant honeys.

1. Newtonian Honeys

Von Fellenberg [1911] was the first to study the viscosity of honey and he used an Ostwald viscometer. He was interested in the adulteration of honey, and found that the addition of corn syrup to honey could be detected by the marked increase in viscosity due to the presence of dextrins in the added corn syrup. EISENSCHITZ [1933] showed that honey diluted with water behaves like a true liquid. In the same year the author commenced his studies into the viscosity of honey and found that, apart from the honey of *Calluna vulgaris*, all the honeys he examined were true liquids and the following are some of the values he obtained.

	% H_2O	η Poises
Canadian sweet clover	16.2	215
Canadian sweet clover	14.5	486
English sainfoin	19.4	53
English lime honey	17.4	87
Californian sage	21.2	28
South Carolina cotton	15.0	275
Mount Hymettus thyme . . .	17.1	174
Connemara fuchsia	18.2	97

The experiments were carried out in a Couette viscometer and in a capillary tube viscometer at 20° C.

It is evident from these results that the viscosity of honey is very markedly influenced by the water content. It is therefore not surprising that many attempts have been made to use the viscosity of a honey as a criterion of its water content as the determination of the latter is not very satisfactory by simple evaporation or by chemical analyses. CHATAWAY [1932] carried out an extensive investigation of the relationship between the viscosity of honey and its water content. She used a falling ball apparatus but, as the ratio of the radius of the ball to the radius of the tube was too high, the rate of fall of the steel balls was not proportional to the square of their diameters. Nevertheless Chataway obtained a straight line inverse relationship between the logarithm of the viscosity and the logarithm of the water content — between the limits 12.8 % H_2O (475 poises) and 22.4 % H_2O (50 poises). It is interesting to note that the data for buckwheat honey did not lie on the straight line.

OPPEN & SCHUETTE [1939] made a further attempt to correlate viscosity and water content used of honey. They a slightly modified GIBSON & JACOBS [1920] falling ball viscometer in which the tube was 21.2 mm internal diameter and the steel balls 0.16 cm diameter.

The viscosities of thirty samples of honey were determined at intervals of 5° C between 30° C and 50° C. The moisture content was estimated by means of the vacuum drying method prescribed by the Association of Official and Agricultural Chemists [1935]. It was found that within the narrow limits of temperature employed, the relationship between viscosity and temperature could be expressed by an equation of the type proposed by ANDRADE [1930],

$$\log \eta_T = a/T + b$$

where T is the absolute temperature and a and b are constants. These results are shown graphically in Fig. 1.

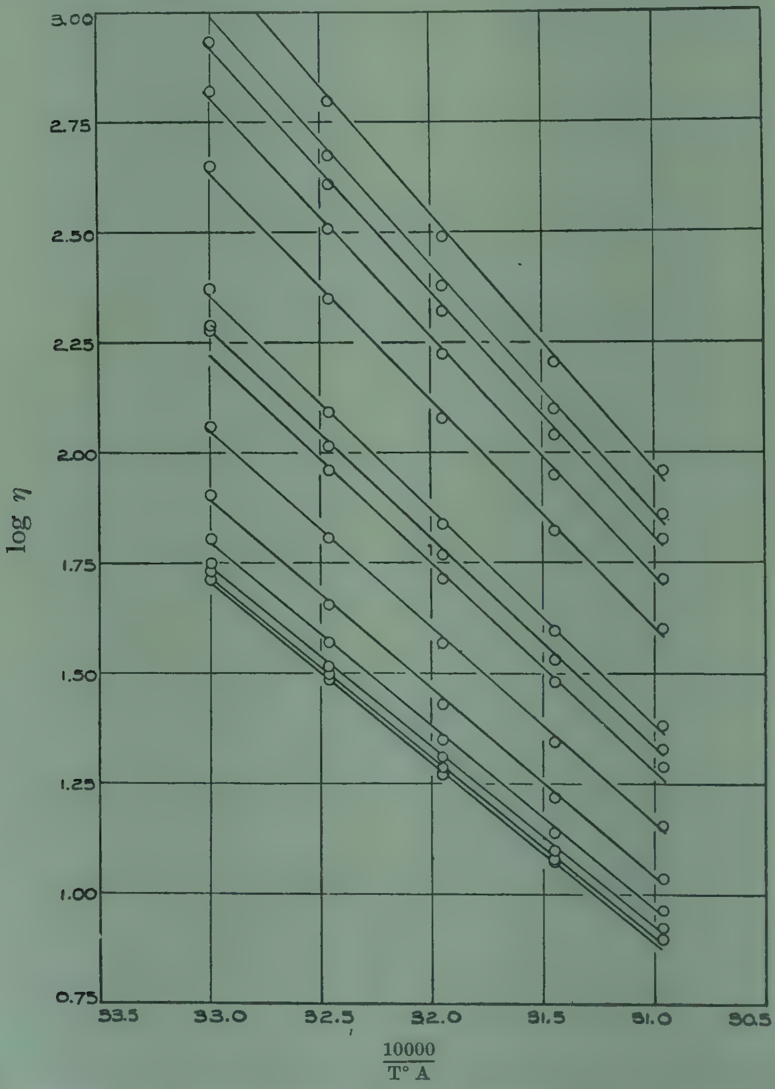

FIG. 1. Effect of Temperature upon Viscosity of Individual Honeys

It was further observed that the reciprocal of percentage water content when plotted against $\log\eta$ for any one temperature gave a straight line relationship; it was found that for the temperature of 40° C (313° A) this relationship could be expressed by the equation:

$$\log \eta_{313} = 42.8\,(16.00 - w)/16.00\,w + 1.676$$

in which w is the percentage water content. The correlation was by no means perfect, as can be seen from Fig. 2.

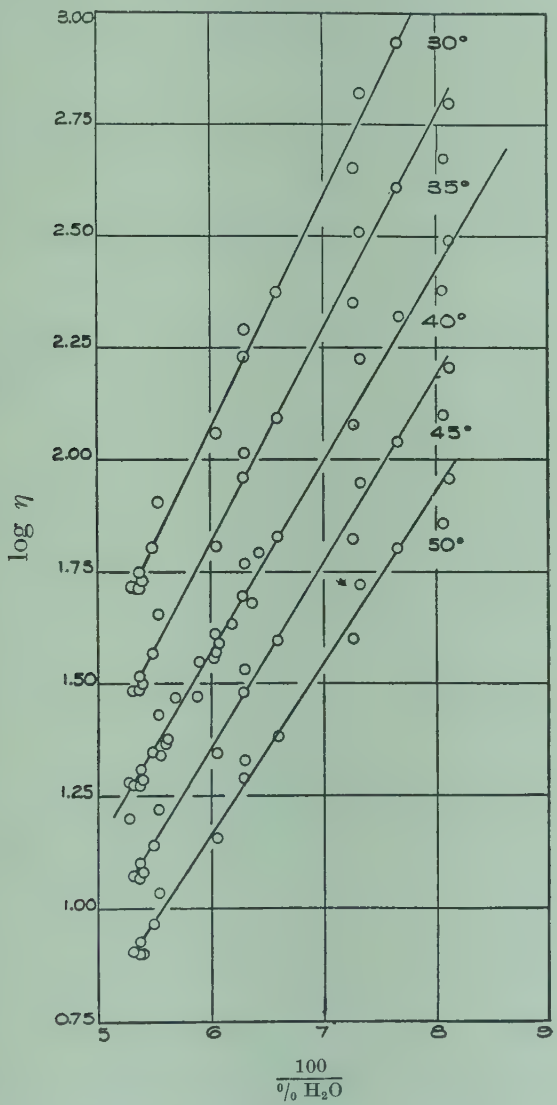

FIG. 2. Variation of Viscosity with Moisture Content at Various Temperatures

Finally, Oppen and Schuette established a general equation correlating moisture, viscosity and temperature by means of which the moisture content could be calculated from the value of the viscosity at a given temperature: —

$$w = (62500 - 156.7\,T)\,[T(\log \eta_T + 1) - 2.287\,(313 - T)].$$

The curves are shown in Fig. 3.

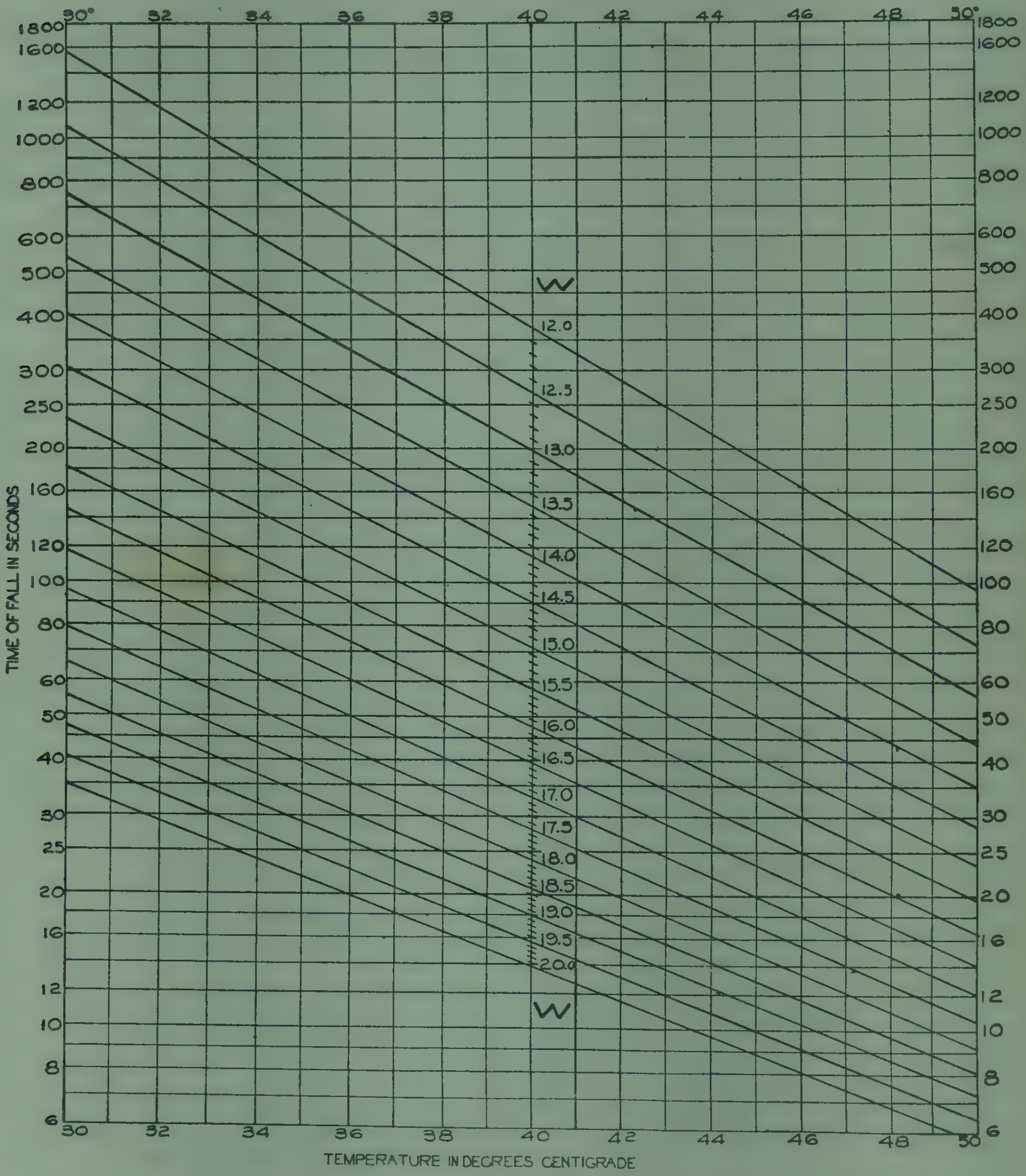

FIG. 3. Direct-reading moisture-viscosity graph

These curves were derived from observations on honey samples ranging in water content from 12.4 % to 19.73 %; a comparison of the results obtained by viscosity measurements and the official vacuum drying method showed that they did not differ, on the average, by more than 0.2 %.

Risga [1937] studied a number of Latvian honeys by means of a Stormer viscometer and found that viscosity of honey was very sensitive to temperature variations. He showed that the decrease in viscosity is very rapid up to a temperature of 40° C. From 40° C to 50° C the decrease is much slower, and above 50° C the decrease is hardly perceptible. There is therefore very little advantage in heating honey above 45° C for the purpose in reducing its viscosity during extracting, or straining or blending. Risga also observed that the viscosity of honeys was not entirely a function of temperature and water content. At the same water content the viscosity of heather (*Calluna vulgaris*) honey is much higher than that of honeys derived from flowers.

Marshall [1938] investigated the effect of temperature and of time upon the quantity of honey extracted from uncapped combs in a honey extractor. He used a Rothamsted radial extractor of 10 inches (approx. 25 cm) radius rotating at speeds ranging from 150 to 460 revolutions per minute. He stored three series of combs overnight at temperatures of 16° C, 22° C and 36° C in extracting rooms kept at the same temperatures. Consecutive extractions were carried out for periods of 30 seconds, 1 minute, 2 minutes and 5 minutes at speeds of 210, 365, 425 and 465 revolutions per minute respectively. The following results are the averages for four combs extracted at the different temperatures:

TABLE II

Percentage Honey Extracted

Temp. ° C	After 1st. Extraction	After 2nd. Extraction	After 3rd. Extraction	After 4th Extraction
16	59.92	24.22	10.53	4.63
22	70.0	21.38	5.25	3.35
36	89.55	7.48	1.54	1.42

Marshall states that, although a higher temperature greatly facilitated the extraction of honey, yet the time required for complete extraction was practically independent of the temperature. Table II shows that the amount extracted in the last five minutes at 36° C was extremely small, so it is possible that the time of extraction could have been reduced without any serious loss of honey. It is very doubtful whether all the honey can be removed from the combs even after long periods of extraction.

Munro [1943] studied the effect of temperature upon the viscosity of a large number of honeys of widely different water content and his results are probably the most extensive yet published. Fig. 4 shows three curves plotted from his data and Table III his results for four representative honeys. Fig. 5 shows the curves obtained by plotting log η against 1/T; it will be observed that the relationship is not a straight line over the wide range of temperatures used by Munro. They are typical of curves obtained for a highly associated liquid (The anomaly shown by curve EE will be discussed later). Munro showed that there are three distinct stages in the effect of

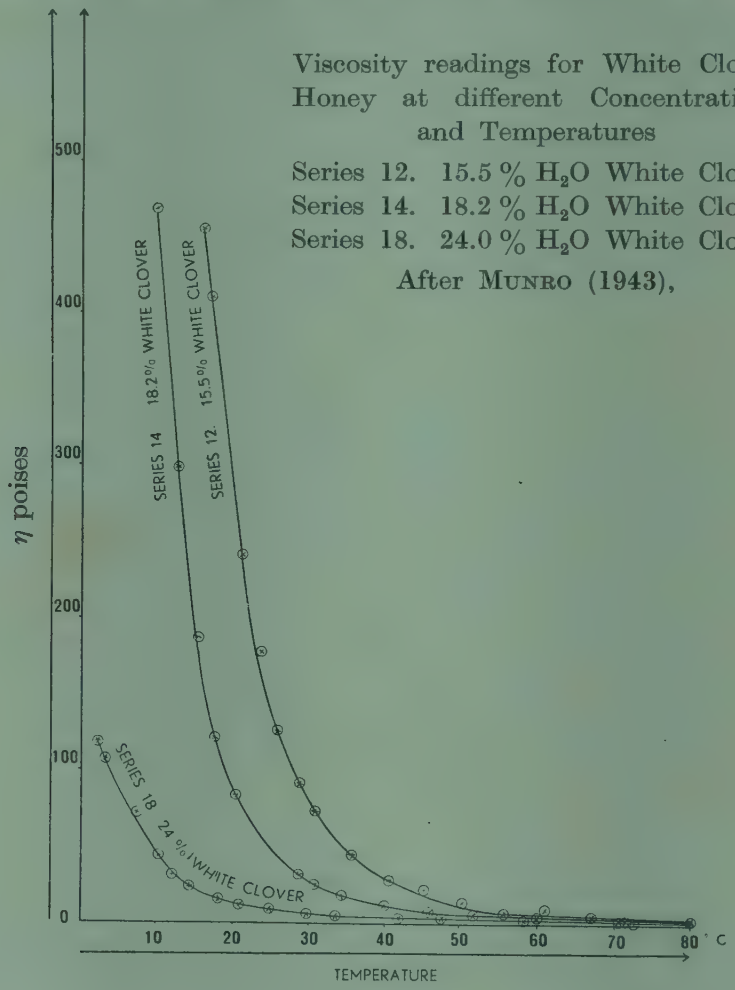

Fig. 4

TABLE III
Relationship between temperature and viscosity of honey
(After MUNRO [1943])

14.2 per cent White Clover		16.1 per cent Sweet Clover		18.6 per cent Sage		24.0 per cent White Clover	
° C	Poises	° C	Poises	° C	Poises	° C	Poises
18.3	801.6	13.7	600.0	6.0	434.4	2.2	120.8
18.6	768.0	14.0	554.4	6.8	400.8	3.4	108.0
18.8	722.4	14.5	511.2	8.9	331.2	4.3	99.2
19.1	674.4	15.0	468.0	9.5	297.6	5.3	88.0
19.6	600.0	15.7	422.4	10.9	249.6	6.4	76.8
20.1	537.6	16.4	343.2	12.1	208.8	7.0	71.2
20.9	475.2	17.5	285.6	13.0	177.6	7.7	64.8
21.7	417.6	18.6	240.0	14.0	148.0	8.4	58.0
23.1	348.0	19.6	211.2	15.4	120.0	9.5	48.0
24.5	288.0	20.6	189.6	16.2	105.6	10.2	44.0
26.6	216.0	21.5	170.4	17.6	91.2	10.7	39.6
27.9	187.2	22.0	156.0	19.2	72.4	12.2	31.2
29.5	151.2	23.1	139.2	20.1	64.8	13.5	25.2
32.0	112.8	24.1	121.2	22.4	52.8	14.2	22.8
33.6	93.6	25.9	97.2	24.0	45.6	16.8	18.0
36.2	61.6	27.3	81.6	26.4	37.2	18.2	15.6
38.2	55.2	29.0	64.8	29.1	28.8	20.9	12.4
41.1	40.8	30.7	55.2	31.9	22.1	22.6	11.6
44.3	28.8	32.0	48.0	36.2	15.6	24.7	9.3
47.2	21.6	35.0	36.0	40.4	9.7	26.1	8.2
48.9	16.8	37.5	25.2	42.6	9.0	28.3	6.9
49.7	14.7	39.4	21.4	44.4	8.2	29.6	6.4
54.1	13.0	41.8	18.2	46.1	7.3	33.3	4.9
58.7	10.3	43.3	16.3	48.2	6.5	38.4	3.8
63.7	7.5	45.4	13.2	53.4	4.8	41.7	3.0
71.5	4.6	48.1	10.7	55.8	3.9	46.9	2.3
76.0	3.5	52.5	7.8	57.2	3.4	47.5	1.8
77.9	2.9	56.3	6.4	59.3	2.9	54.1	1.4
79.1	2.7	65.1	4.0	62.2	2.5	58.2	1.1
79.8	2.5	68.6	3.0	64.7	2.0	62.8	.9
		71.1	2.6	72.1	1.4	66.2	.7
		75.8	2.1	74.1	1.2	67.7	.7
		78.5	1.7	77.0	1.0	70.3	.5
		79.5	1.5	78.0	.9	72.8	.4
				79.8	.8	77.4	.3
						80.0	.3

temperature upon the viscosity of honey: the greatest change occurs as cold honey is being warmed to room temperature, further warming reduces the rate of decrease of viscosity and no advantage is gained by heating honey above 30° C as the decrease in viscosity is of no practical value beyond that temperature. (This temperature differs widely from that given by Risga but it is evident from Munro's data that 30° C is sufficiently high for the extraction and handling of most honeys).

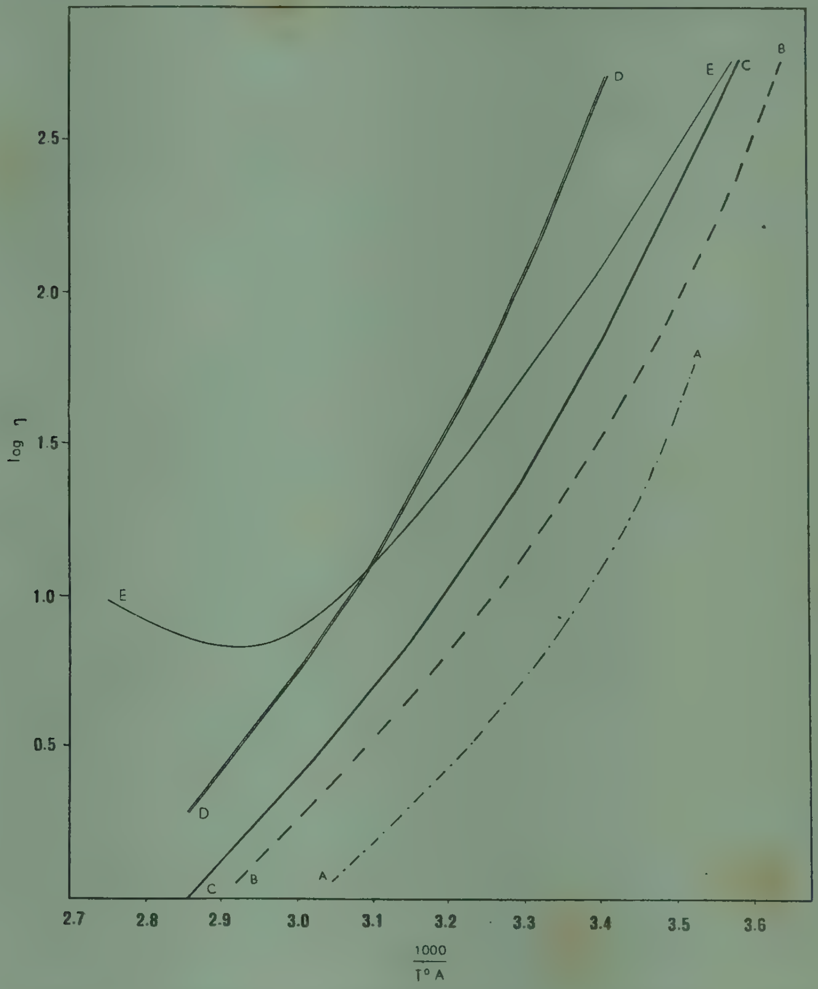

FIG. 5. Influence of temperature on the viscosity of honey

AA = Sweet clover, 24,0 % H_2O
BB = White clover, 20.2 % H_2O
CC = Sage, 18.6 % H_2O
DD = Sweet clover, 15.4 % H_2O
EE = Heather, 20.8 % H_2O

2. Thixotropic Honeys.

It has been known for a long time, ever since Hruschka discovered the honey extractor in 1865, that heather (*Calluna vulgaris*) honey cannot be made to flow from the combs under the influence of the centrifugal force developed in a honey extractor. Its viscosity is too high, therefore the honey is obtained by crushing combs in a press under high pressure. Over sixty years ago, Cheshire made the following statement.

> "The beautiful rich-coloured and highly flavoured honey obtained from the heather, the pride of the Scottish hills, is, for two or three days after gathering, extremely limpid, dropping on the slightest jar from the combs if the latter are held in a horizontal position, yet it becomes so gelatinous when ripened that the contents of a single cell, if successfully removed, will retain its hexagonal figure for some time . . . . . ."

This passage is of great historical interest because it is the earliest recorded description of the peculiar conversion of heather honey from a liquid to the gelatinous state, and because Cheshire described the precise condition which prevents this honey from flowing from the combs in a revolving extractor.

De Boer & Kniphorst [1932] appear to have been the first to investigate the rheological properties of heather honey, although most beekeepers were familiar with the fact that good quality heather honey will set into rigid gel when left at rest but will flow again on stirring. De Boer and Kniphorst measured the viscosity of heather honey in a Holde viscometer and found that its viscosity increases many fold when left ar rest for a period of twenty-four hours: the maximum rate of change in viscosity took place at about 15° C. On stirring, the viscosity returns to its original value. De Boer and Kniphorst described the phenomenon as "thixotropy" as the honey appeared to conform to the definition of thixotropy proposed by Freundlich and Peterfi, namely an isothermal reversible gel-sol-gel transformation induced by shearing and subsequent rest.

Scott Blair [1935] studied the viscosity of heather honey by means of a falling ball apparatus and found that the rate of fall was much higher in a sample immediately after stirring than when the sample had been left at rest overnight. In some samples the ratio of the two rates was as high as 200, compared with a ratio of unity for a commercial brand of sugar-syrup and clover honey when tested under the same conditions. Scott Blair questioned the application of the term thixotropy to the effects he observed as he was unable to show that, after stirring, the honey was a true sol;

neither could he find any well-defined evidence of a yield-value before or after the honey had been left at rest. SCOTT BLAIR & MORLAND [1936] made further experiments with the falling ball method, and they stated that they had found samples in which the rate of fall immediately after stirring was "several thousand times" higher than when the honey had been left at rest overnight.

PRYCE–JONES [1934] examined several samples of heather honey in a torsion viscometer. He showed that all the samples were non-Newtonian fluids and, in addition, that they increased in viscosity when left at rest after stirring, but returned to the original state on stirring anew. The samples showed great variations in viscosity, in their rate of setting into a gel, in their colour and in the period of time before crystallisation, if any, took place. PRYCE-JONES [1936b, 1994b] showed that the gelatinous properties were due to the presence of a protein. On the removal of the protein, heather honey behaves like a Newtonian liquid, but the addition of the protein to clover honey imparts to it all the rheological properties of heather honey. He has examined over three hundred samples described as heather honey, the protein content of these samples varying from 0.20 % to 1.86 %. Pollen analyses indicated that very few of these samples had been derived from heather nectar alone. From various evidences it may be safely assumed that protein content is a criterion of the purity of a sample of heather honey but it is difficult to set a rigid standard. As the sample which contained 1.86 % protein contained no pollen grains other than those of heather, this figure has been adopted as a standard for pure heather honey. As pollen analyses showed, samples containing only 1.0 % or less of protein were mixed with a high proportion of honeys derived from the nectar of other flowers. The protein content can be correlated with the rheological properties and the rate of crystallisation. Pure heather honey remains gelatinous for many years, but if the protein content is less than about 1.0 % crystallisation takes place in a few weeks. If its value is between 1.0 % and about 1.5 % crystallisation is delayed for many months and the crystals resemble small pin-heads which may ultimately grow into spheres 3 or 4 millimeters in diameter. These crystals remain permanently suspended in the remaining gelatinous fluid. Bubbles of air are always present in heather honey: they are unable to ascend because their buoyancy cannot overcome the yield-value of the gel — in this respect heather honey resembles a "thixotropic" gel such as aluminium hydroxide in water containing traces of electrolytes.

Even during vigorous stirring the air bubbles do not ascend, this indicates that the gel structure is not completely destroyed so that it never assumes the sol state. This may be regarded as tentative evidence that heather honey is not a truly thixotropic system according to the original Freundlich–Peterfi definition. More refined measurements confirm this evidence. As is well known, thixotropic systems set into a gel much more quickly in a vessel of small diameter than in one of larger diameter, hence it is not surprising that heather honey sets at a rapid rate in the confined space of a comb cell of which there are about 28 to the square inch (nearly 5 per cm²). The large variations in protein content enables one to obtain a clearer picture of the difference found in the behaviour of heather honey. One other factor must be borne in mind, namely that the protein is precipitated if heated above 65° C, so that heather honeys heated above this temperature possess quite different properties from unheated heather honeys. It is interesting to note that one often finds that prize honeys at Honey Shows have been heated in order to render the gelatinous properties much more pronounced. Most honey judges are unable to detect this treatment; but simple rheological observations can easily detect heather honey heated above 65° C. It has been suggested that heather honey could be separated from the wax cells by heating to a temperature above the melting point of wax — as is sometimes done with very viscous honeys. As the melting point of wax is near 65° C the protein is precipitated, the liquid wax becomes enmeshed within the precipitated protein and does not ascend to the surface of the liquid honey. If the wax does separate, then the heather honey is of inferior quality.

Fig. 6 shows the pattern of the time-deflection curves obtained for heather honey in the PRYCE–JONES [1934, 1936a] electro-magnetic thixotrometer. Briefly, this apparatus consists of a torsion viscometer in which a cylinder, suspended at the end of a torsion wire, is immersed in the honey contained in a concentric cylindrical vessel. The torsion system carries an astatic pair of magnets, one magnet lying in the field of a coil actuated by a battery so that the flow of the current deflects the suspended cylinder through an angle of 25°. As soon as the current is cut off the suspended cylinder begins to return towards the zero position and thus traces a time-deflection curve which is exponential when the cylinder is suspended in a Newtonian liquid. Any departure from the true exponential form indicates that the fluid is not a true liquid. The suspended cylinder can be kept in its deflected position at 25° from zero for any period of time during which it is desired to observe the change in viscosity of a thixotropic system at rest. As soon as the current is cut off the suspended cylinder

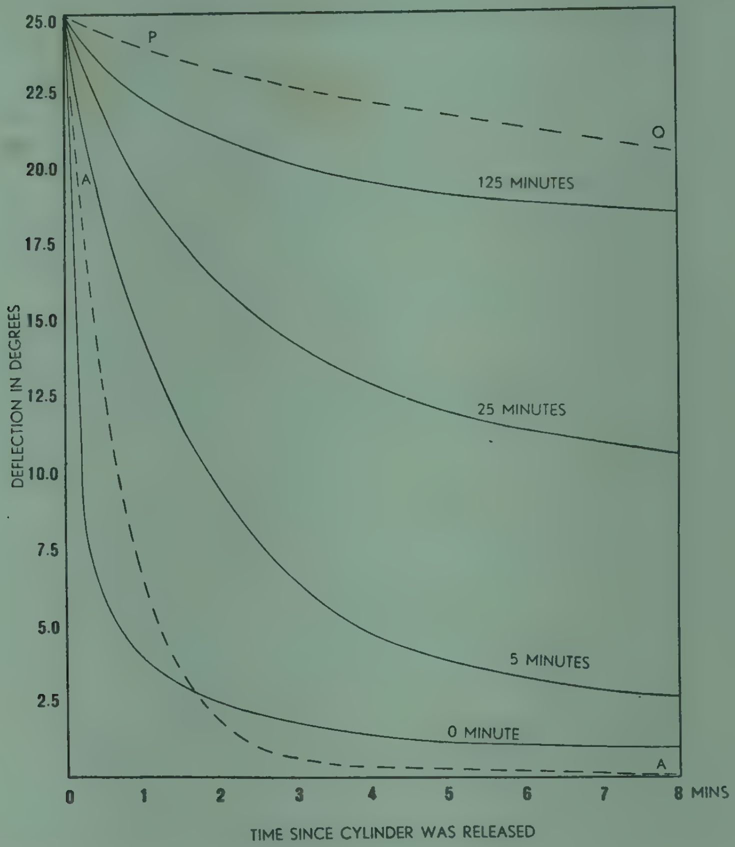

FIG. 6. Time-deflection curves for heather honey left at rest for increasing periods

returns towards zero at a rate determined by the viscosity of the system. Thus the curve "0 minute" shows the time deflection curve obtained when the cylinder is released immediately after stirring has ceased; the curve "5 minutes" after the cylinder has been left at rest for 5 minutes in its deflected position . . . . and the curve "125 minutes" when the cylinder has been left at rest 125 minutes in the deflected position. (The curve A – – – – A corresponds to a true liquid of 200 poises viscosity). It is obvious that there is a marked increase in viscosity during the first 5 minutes, still more so during 25 minutes. It is not possible to deduce whether the curve "0 minute" corresponds to a true liquid, because the sytem has been increasing in viscosity while the curve is being traced. (As shown, the curve is not exponential but, for the reason given, one cannot deduce that the system was not a true liquid at the instant stirring ceased). The curve PQ corresponds to the same heather honey after it had been heated for one hour at 70° C. As already stated, the protein is precipitated at this temperature and the viscosity of the gel is therefore greatly increased. These observations are in agreement with Munro's statement that the viscosity of heather honey increases in the region of 65° C as shown by the sudden rise in the curve EE, relating log η with 1/T in Fig. 5. In order to determine whether a heather honey has been previously heated above the temperature of precipitation of the protein, the honey is examined by the method given above. It is then heated to 70° C for one hour and the test again repeated. If the two curves coincide it may safely be assumed that the honey has been previously heated. If the second curve indicates a much higher viscosity than that observed during the first test then one may conclude that the honey had not been previously heated. One factor, which is not understood, should be borne in mind, namely that the protein in heather honey appears to "age" if the honey is kept for several years. If one examines a heather honey entirely free from glucose crystals, and which has never been heated, after it has been kept for two or three years one obtains a time-deflection curve near the position PQ. Heating to 70° C does not materially affect the viscosity.

The only other honey which possesses marked thixotropic properties is the manuka (*Leptospermum scoparium*) honey of New Zealand; this was discovered almost simultaneously by Scott Blair and the author in 1936. It possesses most of the peculiarities of heather honey, its protein content is in the region of 1.0 % for the best qualities and it resembles heather honey in its type of crystallisation. It is produced in abundance in New Zealand and it is therefore not surprising that after the publication of the fact that manuka honey is thixotropic the author found seventeen samples of English heather honey — which is always sold at a premium price — which contained a large proportion of manuka honey. Fortunately its peculiar triangular pollen grains are easy to identify. It is also of interest that after it became known that the gelatinous structure of heather honey is due to the presence of protein, the author found seven samples of heather honey which contained gelatine! The gelatine content ranged from 0.80 % to 4.3 %. Apparently the gelatine had been added as a solution in water as each of the seven samples contained over 25 % water and all fermented in a few weeks.

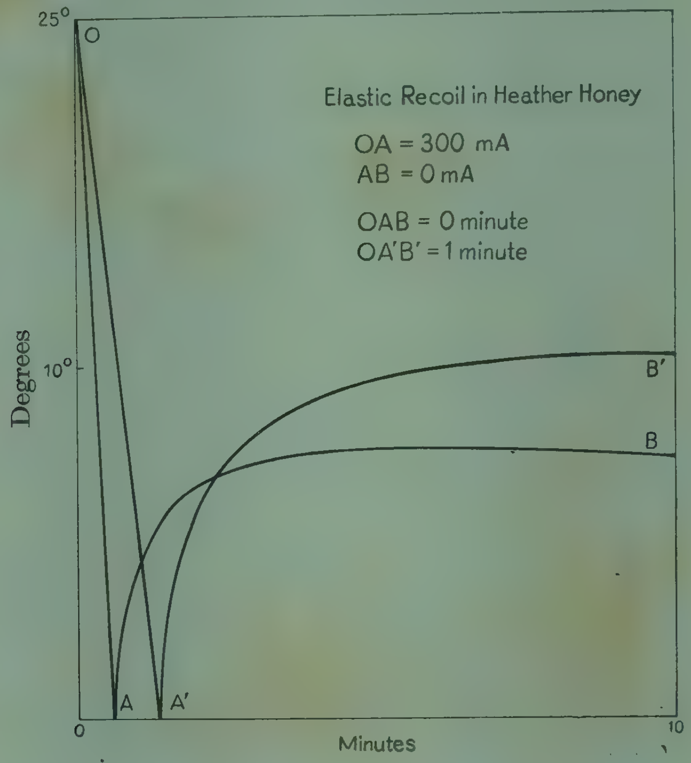

FIG. 7

PRYCE–JONES [1936a, 1936b] discovered another peculiar property of heather honey, as well as manuka honey, which he described as "elastic recoil". This is illustrated, in its simplest form, in Fig. 7 which shows actual photographic records of the curves obtained by means of the electromagnetic thixotrometer already described. A sample of heather honey is placed in the cylindrical container and well stirred by rapid vertical movements of the stirrer. The suspended cylinder is deflected to 25° and the honey again stirred vigorously. The current is suddenly reversed and 300 milliamperes passed through the coil, the cylinder returns to zero along the curve OA. When the spot of light reaches zero the current is cut off — there is a sudden recoil along the curve AB. The experiment is repeated but now the deflected cylinder is kept at 25° for one minute, the current is again reversed and 300 milliamperes passed through the coil and the cylinder returns to zero along the curve OA′, the current is cut off and the cylinder recoils as shown by the curve A′B′. It is evident that a marked change has taken place in the elasticity of the honey during the brief resting period of one minute.

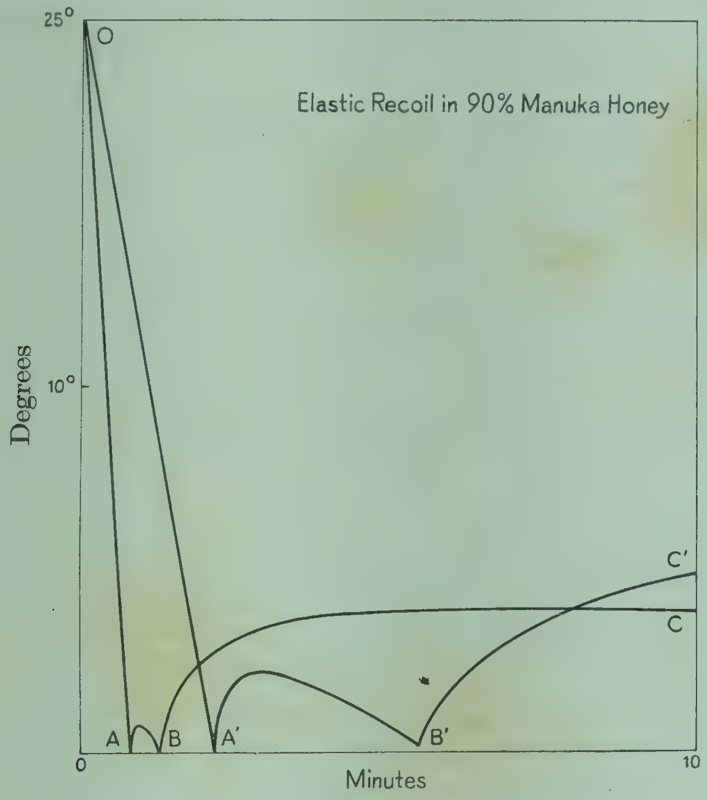

FIG. 8

Fig. 8 shows two curves obtained by a slightly more complicated method. As before, the cylinder is deflected to 25°, the honey is stirred and 300 milliamperes current passed through the coil. As soon as the cylinder has been forced back to zero, at A, the current is reduced to 30 milliamperes, the cylinder recoils against the electromagnetic field induced in the coil and the curve AB is obtained. As soon as the spot of light reaches B the current is cut off completely and there is a sudden recoil along BC. The experiment is repeated by deflecting the cylinder to 25°, the honey is stirred and left at rest for 5 minutes. At the end of 5 minutes the current is reversed and the curve OA′ is obtained, the current is reduced to 30 milliamperes, the cylinder recoils and traces the curve A′B′; the current is then completely cut off and the recoil curve is shown by B′C′. The difference in the area enclosed by the two curves AB and A′B′ shows that there has been an appreciable change in the system during the resting period of five minutes. It has been found that the area enclosed by the curve AB, obtained immediately after stirring, can be closely correlated to the protein content of the honey for the same water concentration. It is of interest to note that the system appears to possess a kind of "memory" as it is able to retain its elasticity during the period required to trace the curves AB and A′B′. The presence of elasticity immediately after stirring indicates that the system is not a sol, but that it still retains a gel structure on stirring. Heather honey, therefore, cannot be a true thixotropic system as it does not conform to the original gel-sol-gel transformation. It appears to be a "false-body" system as defined by PRYCE–JONES [1941], that is a gel which is reduced in viscosity on stirring and regains its original viscosity when left at rest, but never attains the sol stage during shearing. Further evidence for this opinion has been obtained from the results obtained with the twin-Couette viscometer (PRYCE–JONES [1941]).

The twin-Couette apparatus consists of two identical Couette viscometers one of which is mounted vertically above the other. The rotating cylinders rotate in *opposite* directions. The inner cylinders are rigidly connected together by means of a yoke and the whole is suspended by a torsion wire carrying a mirror and its movements are observed on a "lamp and scale" system. The rotating cylinders can be made to rotate at the same speed, or at different speeds in any selected ratio. If, for example, a Newtonian liquid of 100 poises viscosity is placed in the upper cylinder and a Newtonian liquid of 200 poises in the lower cylinder, then if the cylinders are rotating at the same speed, then as the speed is increased the yoke is deflected from the zero position through an angle proportional to the speed of the cylinders so that one obtains a straight line as shown by OA in Fig. 9. If, however, the upper cylinder is filled with a Newtonian liquid and the lower cylinder with a non-Newtonian fluid, one obtains a curve OBC because at the lower rates of shear the viscosity of the non-Newtonian liquid is higher than that of the Newtonian liquid, but at higher rates of shear its structure is broken down so that its viscosity is lower than that of the Newtonian liquid. The curve OBC was obtained by placing a clover honey, of 100 poises viscosity, in the upper cylinder and a heather honey which had been left at rest for 48 hours in the lower cylinder. The rate of shear was gradually increased from 50 sec^{-1} to 900 sec^{-1} over a period of 45 minutes. The curve CDO was obtained by gradually reducing the rate of shear between the same values during the same period. It is evident from the curve CDO that the heather honey after shearing is still non-Newtonian; hence it has not been reduced to the sol state. It is therefore not a truly thixotropic system but corresponds to the definition of a "false-body" system. The curve OG was obtained after the removal of the protein from the same sample of heather honey; the removal of the protein has converted the honey into a Newtonian liquid.

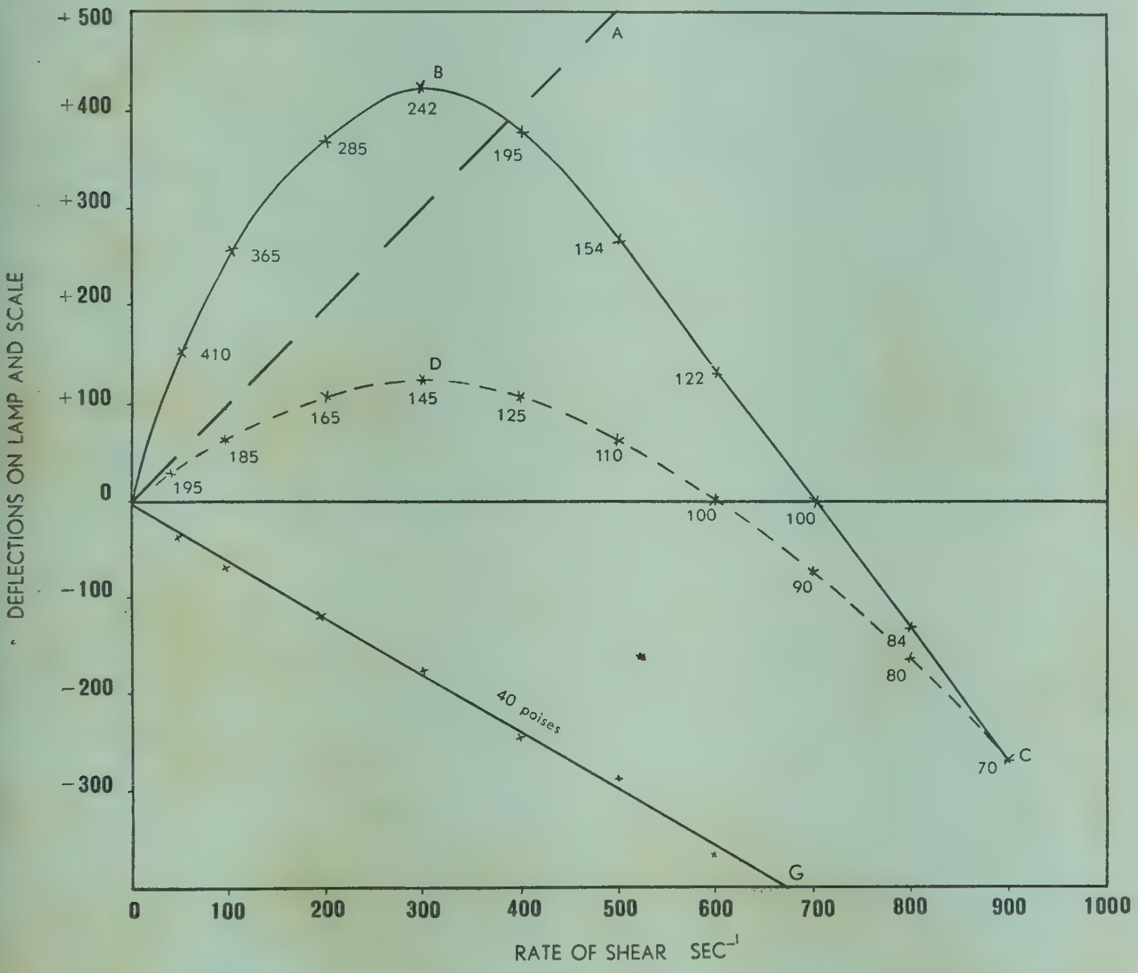

FIG. 9

Parallel results can be obtained by means of a simple Couette apparatus as shown in Fig. 10. The two curves are virtually hysteresis curves (Pryce–Jones [1936a]) for heather honey. The curve AB was obtained by gradually increasing the rate of shear from 50 sec^{-1} to 900 sec^{-1} over a period of 30 minutes, and the curve BC by decreasing the rate of shear from 900 sec^{-1} to 50 sec^{-1} over the same period. The latter curve again confirms the opinion that heather honey is not a true liquid after it has been subjected to a high rate of shear.

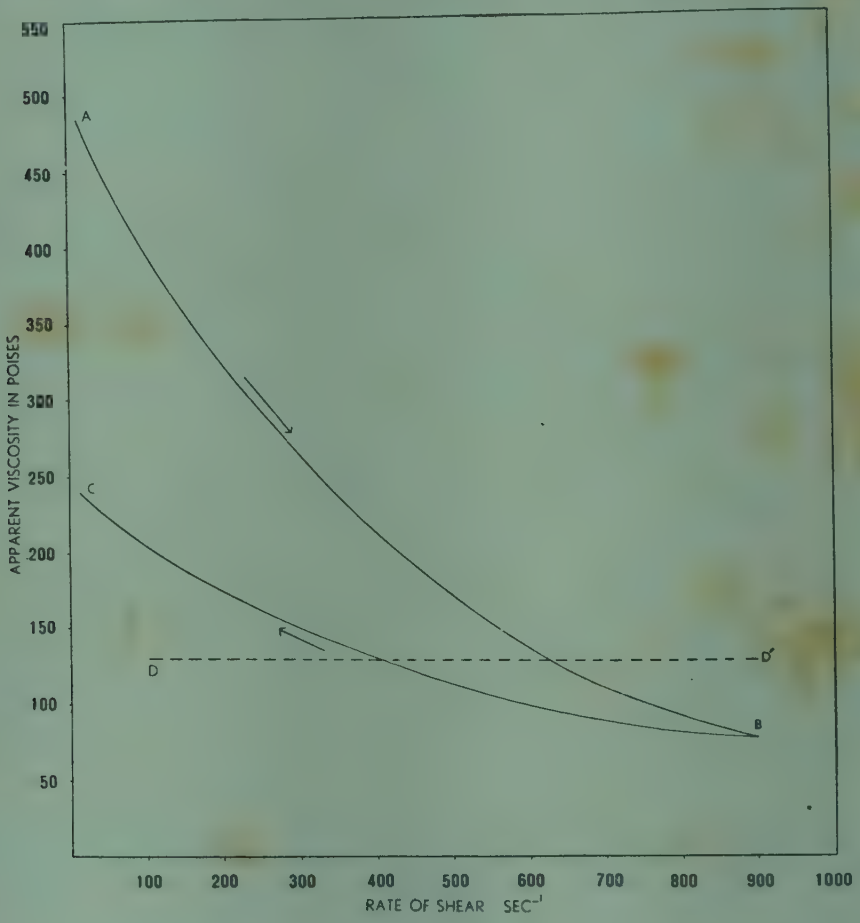

Fig. 10

As these observations on heather honey have all been obtained by means of a falling-ball or rotation, viscometers it is of interest to determine how far they can be confirmed by means of capillary tube viscometers. Scott Blair [1937] designed a simple and ingenious modification of the well-known Bingham and Murray (1923) plastometer. Instead of using the conventional empty capillary tube, he started with a tube full of liquid which is emptied by means of

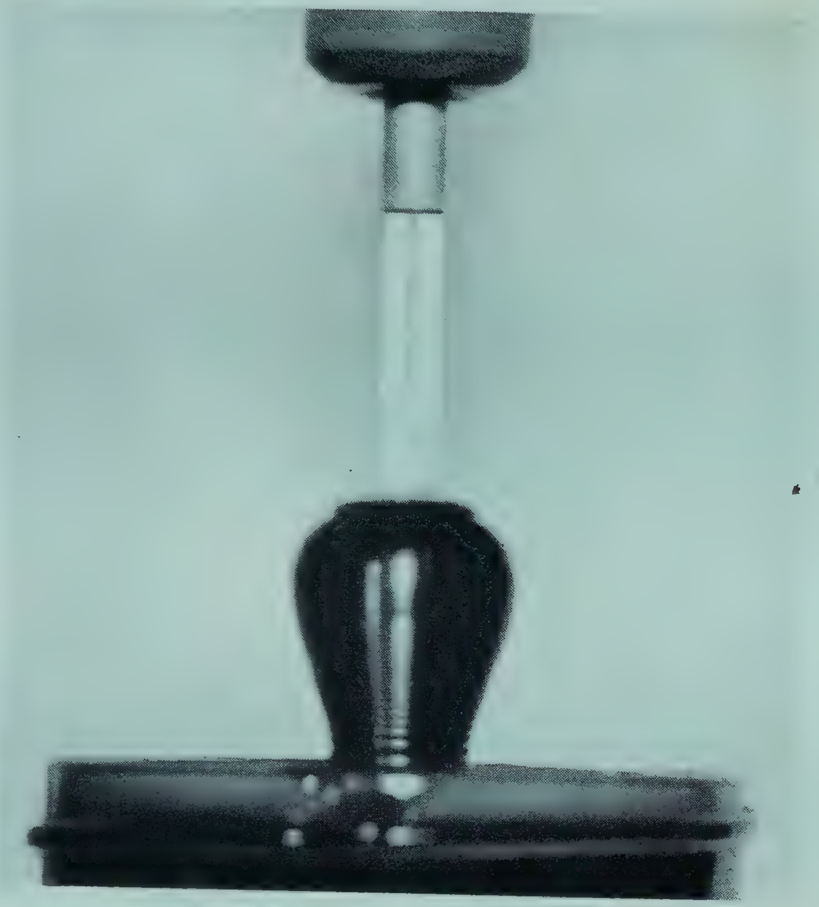

Fig. 13 A. Rod rotated in honey at 60 r.p.m.

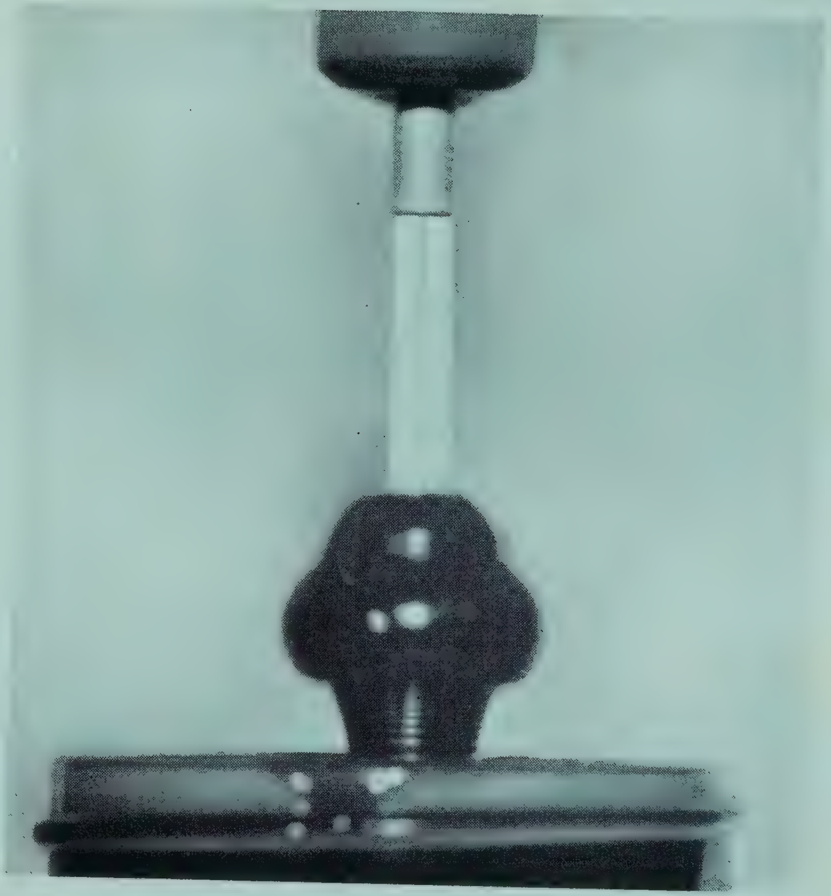

Fig. 13 B. Rod rotated in honey at 90 r.p.m.

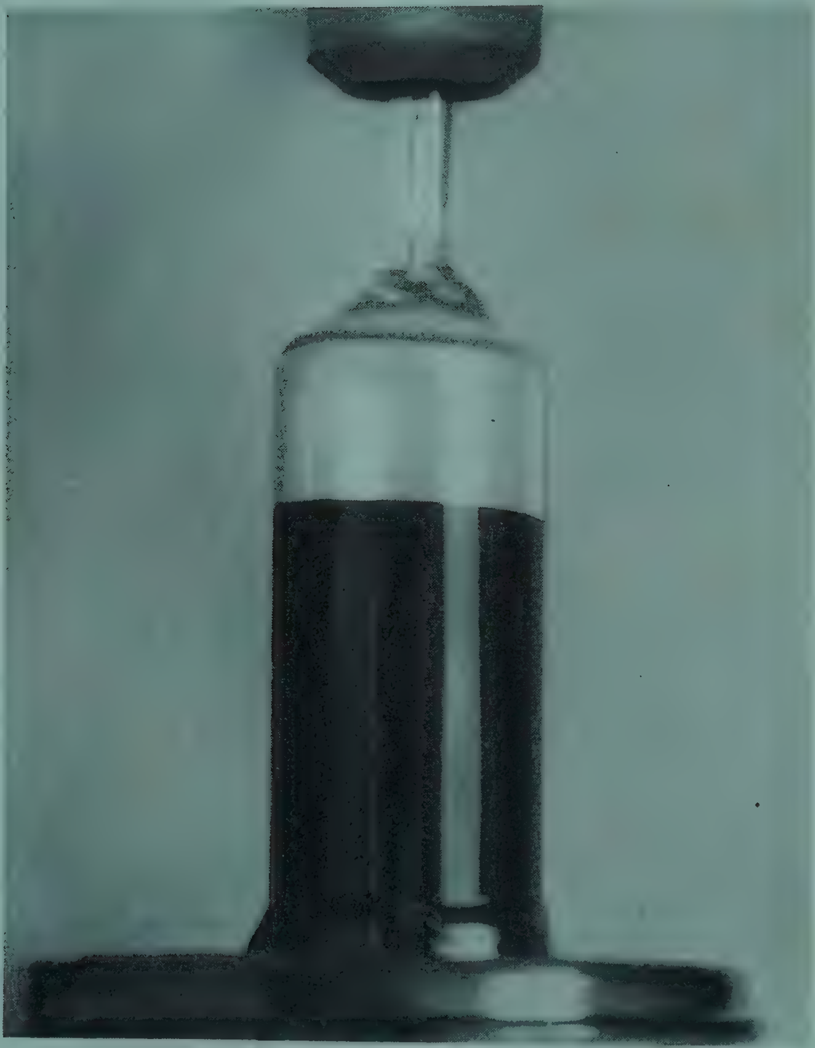

FIG. 14. "Stringy" honey rising up interior of rotated tube

air at constant pressure. Scott Blair examined a large number of honeys, and with the exception of heather honey he found that they were all true liquids. The latter however, gave a velocity gradient — stress curve which was distinctly curvilinear and indicated the presence of a definite yield-value. The value of the viscosity of a liquid in the Scott Blair apparatus is given by

$\eta = Pt.r^2/(L^2 - l^2) \times 4$. Hence Pt is proportional to $(L^2 - l^2)$.

where P is the pressure, t the time of application of the pressure, L the total length of the tube, and l the length of tube filled after time t. The following are three typical results obtained by Scott Blair: —

(1) Willow herb honey: $P = 1.0$

Pt	0.25	0.50	0.75	1.00	1.25	1.50	1.75	2.00
$L^2 - l^2$	19	39	57	77	97	117	137	151

(2) Swiss larch honey: $P = 4.0$

Pt	2	3	4	5	6	7	8	9	10	11	12
$L^2 - l^2$	41	59	79	99	112	135	152	172	194	213	237

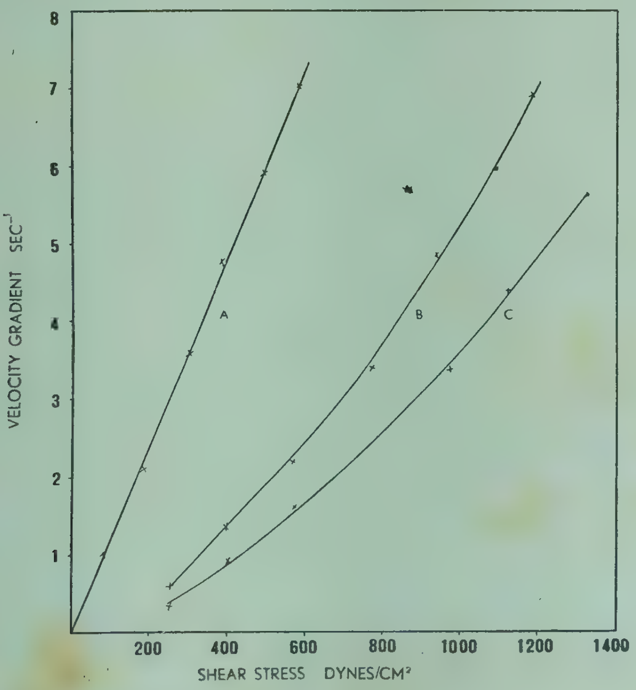

FIG. 11

A. Sample of Clover honey 80 poises
B. Sample of Heather honey after stirring
C. Sample of Heather honey (B) after 12 hours' rest. (Protein = 1.34 % H_2O = 21.6 %) Temperatures 20° C

(3) Heather Honey: $P = 4.5$

Pt	1.12	2.25	3.37	4.50	5.62	6.75	7.88	9.00	10.1	11.2
$L^2 - l^2$	3	8	13	26	42	67	97	131	163	201

It is evident that in the first two honeys that Pt is proportional to $L^2 - l^2$ but that the rate of flow of the heather honey increases much more rapidly than is demanded by this relationship as the tube is emptied; the first two honeys are true Newtonian liquids but the heather honey is an anomalous fluid.

In 1950 Pryce–Jones used a Techne viscometer, described by DE BRUYNE [1949] which is identical with a Bingham and Murray apparatus except that a constant air pressure is maintained by a heavy polished plunger sliding freely in a cylinder which acts as an air reservoir. These results are shown in Fig. 11. where A is a sample of clover honey, B a sample of heather honey immediately after stirring has ceased and C, the same honey after it has been left at rest for 12 hours. It is evident that the clover honey is a true Newtonian liquid, that the heather honey is an anomalous fluid with definite evidence of the presence of a yield-value which increases with time of rest.

3. Dilatant Honeys

The term "dilatancy" was introduced by Osborne Reynolds to describe the property of a granular system, such as moist grains of sand, which increases in volume when sheared laterally. Of recent years the meaning of the term has been expanded to include any system whose viscosity increases with increasing rate of shear beyond a critical minimum value. The system need not contain any solid particles but can a be true solution such as gum arabic in water to which a small amount of borax has been added. The term can therefore be justly applied to honeys which show an increase in viscosity with increasing rates of shear. A large number of such honeys has been found and they were first observed by PRYCE–JONES [1941] by means of the twin-Couette viscometer. For example, a sample of honey from *Eucalyptus ficifolia*, obtained from the neighbourhood of Stellenbosch, Union of S. Africa, possessed the peculiar property of being able to be drawn out into a long string from five to seven feet long (about 2 meters). In other words it displayed the property of "Spinnbarkeit" or "Leptogenesis" (PRYCE–JONES [1944a, 1950]).

The presence of dilatancy in honey is most easily demonstrated by means of the twin-Couette viscometer; it has already been stated that the two rotating cylinders can be made to rotate at different speeds in any selected ratio. Hence if a liquid of 100 poises, for example, is placed in the upper cylinder and a sample of honey in the lower cylinder, then the ratio of the speeds can be selected so that the yoke remains in the zero position for constant speeds of the two cylinders. (It will remain at zero irrespective of the actual speeds of the cylinders if the honey in the lower cylinder is a true Newtonian liquid, so long as the ratio of speeds remains constant. On the other hand, if the honey is not a true Newtonian liquid the yoke will be deflected from the zero position if the actual speeds of the cylinders are changed, because the viscosity of the honey is a function of its rate of shear). Further the viscosity of the honey is inversely proportional to the speeds of the two cylinders; for example if the upper cylinder is rotating at 10 revs. per minute and the yoke is brought to its zero position by rotating the lower cylinder at 2.5 revs. per minute then the viscosity of the honey is 400 poises. A sample of *Eucalyptus ficifolia* honey was placed in the lower cylinder and an oil, a true Newtonian liquid, of 75 poises in the upper cylinder. The lower cylinder was rotated at a speed corresponding to a rate of shear of 10 sec^{-1}; the yoke was brought to its zero position when the upper cylinder rotated at a speed corresponding to 12.5 sec^{-1}; the speeds of the cylinders were then *fixed* in this ratio. The viscosity of the honey at the rate of shear of 10 sec^{-1} is therefore 93.75 poises. The speeds of the cylinders were then gradually increased and the yoke remained at zero until the rate of shear increased to 63 sec^{-1} when the viscosity of the honey suddenly increased and the yoke was deflected to its extreme position. Balance was restored when the upper cylinder was adjusted to 93 sec^{-1} which corresponds to a viscosity of 109 poises. On increasing the rate of shear still further the viscosity increased at a very rapid rate until the honey formed a dome above the fixed cylinder and further observations were therefore not possible. In Fig. 12, A shows the results obtained with *Eucalyptus ficifolia* and B, those with *Eucalyptus eugenioides*. Similar results were obtained with *Eucalyptus corymbosa* and *Opuntia engelmanni* honeys. It is interesting to note that Lovell (1926) states that "the honey of *Eucalyptus eugenioides* is so viscous that it clings to the extractor in thick ropes, which effectually check its revolutions".

This is hardly the correct explanation, as the honey under low rates of shear is no more viscous (86 poises) than a great number of other honeys. The most probable explanation is the development of dilatancy under the high rate of shear induced by the high rate of flow when the honey leaves the extractor.

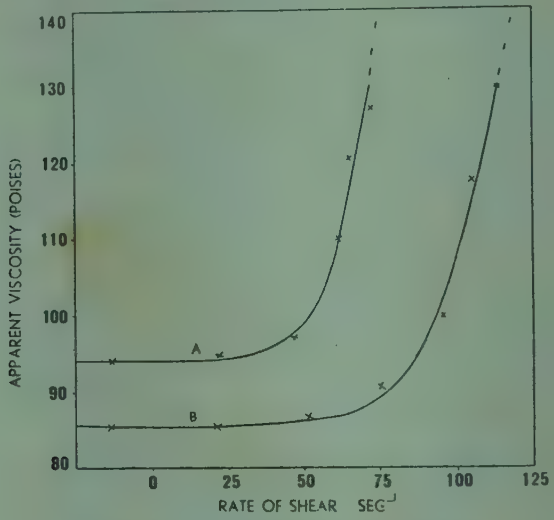

FIG. 12. Dilatancy in honey

A. *Eucalyptus ficifolia* honey 7.2 % dextran
B. *Eucalyptus eugenioides* honey 6.4 % dextran

In 1948 Pryce–Jones found that these dilatant honeys possess a most peculiar rheological property. The effect can be most easily demonstrated by means of photographs which are reproduced in Fig. 13 (Pryce–Jones [1952]). The honey jars contain *Eucalyptus corymbosa* honey and the photographs are almost natural size. A glass rod, attached to a chuck on a variable speed motor, is immersed in the honey to a depth of about 7.5 cm and this is rotated at a gradually increasing speed. In A, the speed is 60 revolutions per minute: the honey has climbed up the spindle and fluted effects can be seen on the surface of the column. In B, the speed is 90 revolutions per minute and the column has assumed the shape of a domed minaret. There is a continuous stream of honey ascending the surface of the glass rod and it appears to overflow at the top and descends in a continuous stream on the surface of the column. In addition there appears to be a procession of ascending fluted surfaces of ever changing pattern. If the speed is increased still further, the centrifugal force sprays the honey into long elastic streamers.

Fig. 14 shows still another peculiar effect. In this experiment a hollow glass tube, 2.5 cm. in diameter is connected to a glass rod which in turn is inserted in the chuck of a variable speed motor. (A small hole is made near the top of the hollow tube to serve as an air escape). The tube is immersed in the honey to a depth of about 10 cm and set in motion at gradually increasing speeds. The honey ascends in the tube as a liquid column and its height is determined by the speed of rotation. The photograph was taken at a speed of 100 revs. per minute. At a speed of 140 r.p.m. the column reached the top of the tube.

Similar results have been described in various colloidal systems by WEISSENBERG [1935, 1947, 1948, 1950] and by GARNER & NISSAN [1949].

PRYCE–JONES [1952] has shown that the fifteen samples of dilatant honeys which he has examined contain dextran $(C_6H_{10}O_5)_n$ in which n is in the region of 8000, and that it appears to be synthesized by *Leuconostoc mesenterioides*. The sample of *Eucalyptus ficifolia* contained 7.2 % of dextran and that of *Eucalyptus eugenioides*, 6.4 %. The dextran can be removed by precipitation with acetone and after the honey has been concentrated to its original concentration, it behaves like a true Newtonian liquid. The peculiar rheological effects can be simulated by the addition of dextran to clover or sainfoin honey.

4. The Effect of Colloids on the Viscosity of Honey

It has been shewn that the viscosity of honey, at a given temperature, is largely determined by its content of water and therefore of its sugar content, but it is evident that certain other components materially affect the viscosity — as has been shown by the removal of 1.5 % or more of protein from heather honey. The pioneer work on the influence of colloids on viscosity was carried out by PAINE, GERTLER & LOTHROP [1934]. They determined the colloid content of 37 samples of American honeys by means of filtration through a collodian membrane, the maximum colloid content of 0.8 % was found in buckwheat honey and the minimum of 0.07 % in mangrove honey. They determined the change in viscosity produced by the ultrafiltration of buckwheat honey and of sumac honey (0.20 % colloid content) at 45° C by means of a Bingham and Green viscometer. They also determined the effects of the rate of shear on the viscosity of the original and the ultra-filtered honeys and compared the results with those obtained with invert sugar. Their results are given in Table IV

TABLE IV

MATERIAL	PRESSURE Cm Hg	VISCOSITY Poises
Buckwheat honey (original)	42.00	4.52
Buckwheat honey (original)	24.66	4.559
Buckwheat honey (filtered)	42.00	4.214
Buckwheat honey (filtered)	24.66	4.234
Sumac honey (original)	42.09	3.686
Sumac honey (filtered)	42.07	3.656
Invert sugar	42.07	3.316

(The solid content of each honey and of the invert sugar was adjusted to 80 %).

Evidently the non-sugar components influence the viscosity of honey, as the viscosity of ultra-filtered buckwheat honey is much higher than that of sumac honey at the same solid concentration, and both were higher than the viscosity of an invert sugar solution at identical sugar concentration. It will also be evident that buckwheat honey shows anomalous viscosity to a small extent. Dr. Paine kindly sent the author a number of the ultra-filtered as well as of the original samples of honey. There were examined in the electromagnetic thixotrometer at a temperature of 20° C and it was found that at this temperature the original buckwheat honey was a highly anomalous fluid. It showed slight indications of thixotropy and these were much more pronounced after the sample had been heated to 70° C for an hour. All the ultra-filtered samples were true liquids. The process of ultra-filtration did not remove the dextrins: all the ultra-filtered samples when tested by the author by dilution with methyl alcohol gave a heavy precipitate. As indicated by PAINE, GERTLER & LOTHROP [1934] this is not surprising because BARCHALL [1908] had shown that honey dextrins possess a molecular weight around 500, that is they are comparatively simple substances of the same order of molecular weight as the tri-saccharides.

LOTHROP [1939] continued his investigations of honey colloids and he gives some most interesting figures for the "Undetermined Content" (or "Organic non-sugars", as he describes them) of several American honeys. Typical examples are given in Table V

Lothrop points out very convincingly that there appears to be no relationship between the quantity of colloids present in honey and its effect upon viscosity as can be seen from the following observations on the original and ultra-filtered samples as shown in Table VI

TABLE V

Type of honey	"Organic non-sugars" %
Buckwheat	6.83
Sumac	8.34
Orange	5.11
Tarweed.	14.50
Hawaiian honeydew . .	8.99
Sourwood	7.38

TABLE VI

HONEY	% Colloids	Viscosity in poises Original	Colloid free	% Reduction
Buckwheat	0.80	4.03	3.88	3.7
Sumac :	0.19	4.11	4.06	1.2
Orange	0.09	3.13	2.85	8.9
Tarweed.	0.18	4.74	3.82	19.4
Honeydew	0.28	4.39	3.75	14.6
White sage	0.12	3.29	2.94	10.6
White clover	0.18	3.31	3.05	8.4
Sourwood	0.15	3.73	3.49	6.4
Invert Sugar			2.45	

All samples were adjusted to 80 % solid content, temperature 45° C.

The variations in the composition of the colloids must therefore be a very important factor in their effect on the viscosity of honey — as the author found in comparing buckwheat and heather honeys at the same protein content.

Lothrop removed the honey dextrins, by means of alcohol, from colloid-free ultra-filtered samples and found, for example, that the viscosity of a sample of sumac honey, containing 5.06 % dextrin, reduced its viscosity by 18.4 %. He suggested that the high viscosity of honeydew honeys is therefore due to the high percentage of dextrin. The author measured the viscosities of seven honeydew honeys and found that they were abnormally high for a given water content, for example the sample G in Table I which contains 11.3 % of dextrin and a water content of 19.3 % had a viscosity of 193 poises compared with a viscosity of the order of 40 to 50 poises in a white clover honey of the same water content.

Lothrop makes a brief reference to the effect of viscosity upon the hygroscopic properties of honey — a factor of great importance when honey is added to bread or tobacco — and states that there exists a definite relationship between viscosity and hygroscopic properties. As examples, he maintains that tupelo and buckwheat honeys, which are higher in viscosity than clover and alfalfa, also possess more marked hygroscopic properties. It is not easy to see the reason for this relationship and it deserves further investigation.

CHAPTER VII

THE RHEOLOGY OF CERTAIN MISCELLANEOUS FOOD PRODUCTS

BY

H. G. HARVEY

THE BRITISH FOOD MANUFACTURING INDUSTRIES RESEARCH
ASSOCIATION, LEATHERHEAD, ENGLAND

0. Introduction

The deformation and flow properties of any material may, in general, be considered to arise from the interplay of two factors; the nature of the operative forces and their mode of application; and the structural composition of the material acted upon by the forces. Knowledge of both these factors is required in order to understand and predict the rheological behaviour of materials in any given circumstances. In view of the diverse nature of many of the foods to be considered in this review, it seems particularly desirable to stress the nature of their structural compositions since their modes of behaviour under the application of similar forces may then be more clearly appreciated despite the more obviously (visual and tactual) different characteristics of the various foodstuffs.

It is therefore proposed to discuss the behaviour of the different foods such as sugar confectionery, chocolate, jellies, sauces, etc., so far as is practicable according to the number of "phases" present which characterize their structural composition. The term "phase" in this connexion will not be defined with rigour but will generally be understood to refer to those constituent portions which are recognizably different in physical form and are separately bounded.

This definition of a "phase" is still far from precise and too much merit clearly need not be expected from such a classification by phases of the different foodstuffs with which we are concerned. Gels and aqueous solutions of polymers present obvious cases of difficulty in respect of their classification as single or two phase systems.

It will be only too apparent to the reader that, for many of the foodstuffs considered in this review, there is a dearth of sound rheological measurements. With a number of the systems considered, there is however, by contrast, much more evidence of the nature of their structural compositions and some clarification of this aspect may perhaps serve as a stimulus to more intensive scientific study of their behaviour under deforming forces.

1. Single Phase Systems

1. 1. *Confectionery Syrups*

Sucrose, invert sugar and confectioners' glucose are three raw materials basic to the sugar confectionery industry and the rheological properties of their syrups and mixed syrups are of prime importance. Confectioners' glucose is a product of fairly closely constant composition obtained by the controlled hydrolysis of starch. Such "glucose" consists of 18 — 19.5 % water with, dissolved in it, the sugars dextrose and maltose together with dextrins.

These confectionery syrups are typical Newtonian liquids and solutions of sucrose have been proposed by BINGHAM & JACKSON [1917] as liquids suitable for the calibration of viscometers.

Sucrose solutions show the characteristic viscous behaviour of non-electrolyte solutions in that their relative viscosity falls with rising temperature: see, for example, HATSCHEK [1928]. HINTON, COULSON & GROVER [1929] have measured the viscosity of individual solutions of sucrose, invert sugar and confectioners' glucose of high concentrations (66 — 78 % solids concentration) by means of the falling sphere method. A simple linear relation was found to exist in the case of each sugar between the logarithm of the viscosity and the concentration of soluble solids, when the latter was expressed as the ratio of weight of sugar dissolved by unit weight of water. The variation of viscosity with temperature was examined over the range 15° C to 26° C and expressed as a simple quadratic equation connecting the logarithm of the viscosity with the temperature. Combined equations were also worked out for each sugar, giving the viscosity of any solution within the ranges of temperature and concentration studied. A simple relationship was found to exist between the viscosities of sucrose and invert sugar solutions in that the ratio of the percentage concentrations by weight of a sucrose and an invert sugar solution having the same viscosity is expressible by a constant factor. The relation between viscosities of sucrose and confectioners' glucose solutions was not found to be so simple and the "constant" factor showed variation between narrow limits.

The same authors measured the viscosities of solutions containing mixtures of sucrose, invert sugar and confectioners' glucose and showed that the relations between the viscosities of solutions of the individual single sugars could be applied to the calculation of the viscosities of the solutions of mixed sugars.

Taimni [1928] also studied the viscosity of concentrated sucrose solutions (70 — 78 %) over the temperature range 30° C to 50° C by means of a capillary tube method. His results are in close agreement with the extrapolated results of Hinton, Coulson and Grover (loc. cit.).

1. 2. *Syrups containing Gelatine*

The viscosities of mixtures of a number of different samples of gelatine with sucrose and with sucrose and confectioners' glucose have been determined by Taylor & Hinton [1941] over a wide range of varying conditions employing the falling sphere technique. The factors explored comprised variations in total solids concentration, gelatine concentration, temperature and pH. It was found that, for mixtures containing a constant proportion of gelatine by weight and constant proportions of non-gelatine dissolved solids, there exists, at constant temperature, a simple linear relationship between the logarithm of the viscosity and the concentration of total solids (including gelatine) when this latter is expressed in terms of weight of total solids per unit weight of water. The magnitude of the change in the logarithm of the viscosity produced by a given change in total solids concentration was substantially the same for all the samples of gelatine examined.

It was also found that the variation in viscosity produced by the substitution of one gelatine sample for another was small by comparison with the magnitude of the viscosity increment contributed by the incorporation of any one gelatine sample, and small also in comparison with the variations produced by changes in the concentration of total solids.

The variation with temperature of the viscosity of mixtures of gelatine with sucrose or with sucrose and glucose was shown to depend upon the original viscosity of the mixture but not upon its composition.

At constant total solids concentration there was found to be a simple relationship between the logarithm of the viscosity and the percentage of gelatine by weight. The slope of this line was less in the case of mixtures containing confectioners' glucose.

The shape of the viscosity — pH curve for solutions of mixtures of gelatines with sucrose, and with sucrose and confectioners' glucose was found generally to be similar to that of the viscosity — pH curve of aqueous gelatine solutions. The actual magnitude of the variation involved was, however, much greater. The variations were certainly not due to the sugar alone since it was shown that a solution of sucrose alone does not show any considerable variation of viscosity with pH.

Taylor and Hinton also devized a method for comparing quantitatively the viscosities of different gelatine samples when incorporated in sugar syrups and the method has been applied to the calculation of the viscosities of gelatine and sucrose together in solution. Such a quantitative comparison might well be of value in the grading of gelatines for many confectionery purposes.

1. 3. *Highly Boiled Syrups* ("*Boiled Sweets*")

Ordinary high boiled sweets may be considered as highly supersaturated syrups of either sucrose plus invert sugar or sucrose plus confectioners' glucose. In the latter case some degree of inversion inevitably occurs during the boiling of the mixed syrup and the invert sugar formed in this way may be as high as 5 % or even higher if acid conditions are permitted. Normally the water content of such boiled sweets is well below 4 % and often below 2.5 %.

If the proportions of "glucose" solids, invert sugar, and water, are maintained within certain limits, then on cooling, such highly supersaturated "syrups" possess the rigidity of solids and when stored under appropriate conditions are quite stable over long periods with little or no tendency for crystallisation of sucrose to take place.

No record of rheological measurements on these highly interesting systems appears to have been published but the qualitative behaviour of boiled sweets at high temperatures (i.e. immediately after their preparation and involving the range 130° C if under vacuum, to 160° C when "boiled" under atmospheric pressure) would seem to be similar to that of similarly composed syrups of higher water content. The low water content of boiled sweets would seem simply to have conferred upon them a much higher viscosity than is shown by the corresponding syrups of higher water content. Thus, when hot, the mass of "boiled sugar" may be drawn out into long threads which may be considered equivalent treatment to forcing a viscous liquid through a tube of decreasing diameter. The material also shows no apparent elastic behaviour or deformation although if emulsified fat is present as in toffee (see later) then elastic behaviour may sometimes occur between appropriate temperature limits.

The high stability of boiled sweets towards the onset of sugar crystallisation ("graining") has been explained by CAMPBELL & CLOTHIER [1926] in the following way.

If the boiled sweets are subjected to a moist atmosphere they will at once begin to absorb a surface layer of water which then dilutes the highly concentrated non-crystalline matrix of sugars and water and the resulting lowered viscosity of the surface syrup film then permits the initiation of crystallization of sucrose. Once crystallization has started, then the fall in concentration of the "syrup" in the neighbourhood of the crystals will again facilitate further crystallization by means of the reduced viscosity. In this way crystallization may spread from the outer surface of the sweets throughout the whole interior. Some confirmation of the part played by the viscosity in affecting the rate of crystallization is afforded by the fact that "graining" proceeds more easily in sugar-invert sugar boilings than it does in sugar-glucose sweets.

As is to be expected the amount of residual water in the boiled sweets is a serious factor in accelerating or retarding crystallization of the sucrose. With very low water contents (below 1.0 %) coupled with suitable protection from atmospheric humidity such confections have been known to remain free from crystallization for many years. If, however, the water content is high, then granulation may occur no matter how carefully the sweets are protected from the atmosphere. In this connection it is necessary to appreciate that the relative vapour pressure of boiled sweets is generally in the range of 25—30 %; so that on exposure to an atmosphere of relative humidity in excess of this range (25—30 %), absorption of moisture by the sweets from the atmosphere, will always tend to take place.

The explanation put forward by Campbell & Clothier (loc. cit.) does not fully explain the resistance of boiled sweets to the onset of crystallisation. Thus it is known that if the proportions of invert sugar or glucose be reduced below certain respective minimum levels then the sweets will readily crystallize. If, however, the proportions of these ingredients exceed certain maximum limits, then the sweets will not crystallize at all but will simply form progressively weaker syrups with continued absorption of moisture.

2. Gels

2. 1. *Pectin Jellies, Jams and other Fruit Preserves*

Pectins are generally regarded as the substances or mixtures of substances extracted from fruits and some other portions of plants, by suitable means, which in association with sugar and acid, or the acid juices of fruits form gels. Thus obtained, pectins appear to consist of long chains of polygalacturonic acid in which the carboxyl groups are esterified with methyl alcohol in varying degree, while the remaining non-esterified acid groups are present either wholly as acidic carboxyl groups or partially in salt formation with metals such as sodium, potassium, calcium and magnesium. The polygalacturonates are of varying chain length (varying molecular weight) and generally contaminated with closely associated arabans, galactans and occasionally other polysaccharides. The pectins, both in respect of their chemical nature and jellying properties have been most extensively studied and in a review of this character it is only possible to give a brief sketch of their most important features. For more detailed and comprehensive information the reader is referred to the textbooks by KERTESZ [1951], MAAS [1951], and HOTTENROTH [1951], the monograph by HINTON [1939] and a thesis [1951] by the author. In this last publication the measurement of the rheological properties of gels is discussed at some length and the interpretation of the concept of gel strength as a combination of viscous and elastic behaviour is advanced.

CHEFTEL & MOCQUARD [1947] devised an apparatus which permitted of the continuous recording of the rheological properties of a gel but which was otherwise very similar to the Campbell jelly tester (CAMPBELL [1923]). These investigators reached the conclusion that while gelatine and similar gels (agar, and silicate gels) possess true elasticity within the sensitivity of the instrument, pectin gels of the normal high sugar — high methoxyl type do not. This difference in behaviour was shown not to be due to the high sugar content since both gelatine and agar gels prepared with a similar concentration of sugar exhibited no qualitative change in behaviour. The pectin gels underwent an initial relaxation when subjected to small stress followed by an increased resistance until ultimately the gel was ruptured. Cheftel and Mocquard found that total disruption of the pectin gel always occurred no matter how small the applied stress, provided the time of application was long enough. Their results were, however, subject to a marked lack of reproducibility between duplicates and it appears that they encountered considerable difficulty in the avoidance of air bubbles in the pectin gels. It is also possible that variations in the preparation and ageing conditions of the gels may have accounted for some of the anomalous behaviour found.

HARVEY [1951] from a review of the evidence bearing upon the elastic and viscous properties of pectin gels reached the conclusion that pectin gels exhibit a far higher degree of viscous behaviour than do gelatine gels.

The mechanism of pectin-sugar jelly formation under different conditions of pH, concentration of pectin and soluble solids etc., has been explained in a *quantitative* manner by HINTON [1940] on the basis that jelly formation occurs as the result of precipitation of a part of the pectin present, in such a way that the large binding surface forces then developed hold the solution of other ingredients (and the remaining soluble pectin) with sufficient power to confer on the whole system the rigidity and normal physical characteristics associated with a jelly. This precipitation of the pectin is considered to occur when the non-ionized pectin present exceeds a certain minimum quantity (i.e. the saturation solubility of the non-ionized pectin) and it is only this excess which is precipitated. Hinton further showed that the amount of non-ionized pectin present in a system can be calculated from a knowledge of the pH, the dissociation constant of the pectin, and its concentration. He found that the rigidity of pectin gels was proportional to the amount of pectin precipitated.

The temperature at which pectin jelly formation first commences has been shown by HINTON [1950] to be a determinate physical property, whereas the setting time is only a secondary property which is dependent on temperature conditions. It was found that, as with jelly strength, pH conditions are a primary factor in regard to setting temperature, increase of pH causing a rapid fall of the latter. Soluble solids concentration, pectin concentration, nature of buffer cations and heating all have subsidiary effects. Hinton concluded that the setting temperature did not appear to be related to the jelly strength in any direct way, as judged by a comparison of the effects of the factors studied on the two properties.

Harvey [1950] pointed out that the concept of setting temperature of pectin-sugar jellies followed directly from the dissociation hypothesis of Hinton [1940] and that the dependence of the setting temperature upon such factors as pH value, pectin and soluble solids concentrations, is accounted for.

By means of a slight modification of Hinton's theory, Harvey was able to provide a quantitative explanation of some of the differences in jellying behaviour caused by different metallic buffer salts. The modified theory was also shown to lead to a simpler conception of effective ionization and this in turn was used to account for some of the differences in jellying behaviour brought about by alterations in the degree of esterification of the acid groups of the pectin molecule.

Earlier studies of the strength of pectin jellies (e.g. Campbell [1923] and Lampitt & Money [1937]) have indicated that upon ageing, the rigidities of such jellies may increase. Harvey [1951] in an experimental study of the effects of the conditions under which pectin-sugar gels are allowed to set has shown that the gel rigidity is unaffected by the rate of cooling during setting but can be markedly increased by storage. At low temperatures (0° — 4° C) the change is small and the rigidity becomes constant after about 48 hours. At higher temperatures (22° C, 27° C, 36° C, and 55° C) of storage the rigidity increases logarithmically with time, often up to an observable maximum value, and then gradually declines. The increase in gel strength is accompanied by a rise in the melting point of the gel, but is substantially unaffected by wide variations in the total concentration of soluble solids, the pH of the gel, and its initial rigidity. The observed maximum rigidity generally increases with a rise in the storage temperature and is attained in a shorter period than at lower temperatures.

The underlying causes of these phenomena have been discussed by Harvey in the light of the conditions for rubber-like elasticity postulated by Treloar [1949] and utilized by Ward [1951] in respect of gelatine gels. It would appear that if pectin chains are precipitated in gel formation, their chemical nature and spatial configurations are in accordance with a certain degree of elastic behaviour. The presence of the entrapped liquid phase in the gel may also be expected to confer additional properties of a plastic nature along the lines indicated by Poole [1925].

It was considered that during the heating of the hot jellying mixture, precipitation of increasing amounts of non-ionized pectin as a three dimensional network takes place in the presence of restrictive forces, due largely to increasing viscosity of the enmeshed liquid phase. Free orientation of the precipitated pectin chains into their most stable configuration may also be hindered at the lower temperatures. On subsequent warm storage at any particular temperature a certain fraction of the pectin previously precipitated at the lower temperature will dissolve while the remainder will be more favourably situated to rearrange itself, over the required time interval, into a configuration of greater stability. The pectin chains in their final arrangement may be expected to present a greater resistance to deforming forces (gel strength) than when present in the gel in its initial state and so afford an explanation of the increase of rigidity observed. Upon subsequent cooling of the gel the pectin which passed into solution will be reprecipitated in a spatial arrangement largely determined by the more stably re-orientated network of pectin chains already present as a result of warm storage. The general process would not be expected to be dependent, in any direct way, upon pH conditions, in accordance with the experimental results obtained by HARVEY [1951].

The rheological properties of a jam or other fruit preserve are very largely those of the pectin-sugar-acid gel but a number of special features do appear to arise from the presence of the natural fruit juice as distinct from the use of purified fruit acids (mainly citric) and their salts. The setting temperatures of jams or jellies made with fruit juices have been found by HINTON [1936] invariably to be appreciably higher than those of jellies made from the corresponding fruit pectin but without the depectinized fruit juice. This phenomenon is believed to be due partly to the presence of salts of lime, magnesium and potassium but investigation of the setting temperatures of pectin-sugar jellying mixtures in which citric acid and citric salts of these metals were employed as buffers led Hinton to the the conclusion that there is some other contributing factor or factors, not at present known.

It also seems possible that there is a special "fruit juice" effect in respect of the wide range of pH over which jams may form a satisfactory "set" although this phenomenon has been reproduced in appreciable degree with buffered pectin-sugar-gels and explained by HINTON [1940] and HARVEY [1950].

The texture of the gel obtained in fruit preserves has been shown by HINTON [1936] to be largely a matter of whether the hot jellying mixture as filled in to the final container is above or below the setting temperature. If the liquid jam is above the setting temperature when filled out, then, with adequate cooling, a clean-cutting, non-sticky gel will form; while should the temperature at the pouring stage be below the setting temperature, then a "broken" or "curdled" or even completely liquid set, will result. Occasionally the setting temperature of jam may be so high as to prevent the production of a satisfactory jellied set even when the liquid jam is filled out immediately after the conclusion of boiling. In such cases, lowering of the boiling temperature or modification of the pH of the jam may be necessary.

HARVEY [1948] has shown that the setting temperature phenomenon may be utilized as a basis for an improved rapid method of cooling of jams.

Jams are known sometimes to exhibit syneresis but no serious published investigations of this phenomenon have been traced.

2. 2. *Gelatine Gels and Table Jellies*

A wide range of types of instruments has been employed by different investigators in the measurement of the so-called strength of gelatine gels and has been reviewed by the author [1951]. Such gels tend to exhibit both elastic and viscous behaviour but generally gelatine gels are more elastic in character than pectin gels.

The strength of gelatine gels is affected not only by the concentration of gelatine but by such factors as pH, type of gelatine, and other dissolved solids, such as sugars.

FERRY [1948a] has measured the rigidities of gelatine gels by using the wavelength of transverse vibrations in a set gel and has shown that a constant value for the rigidity was reached more rapidly if a given temperature was approached from a lower rather than from a higher temperature. Ferry's results, confirm the need found earlier by LAMPITT & MONEY [1936], for adequate time to ensure that the maximum rigidity has been reached. Both Lampitt and Money (loc. cit.) and FERRY [1948b] have shown that the rigidity or strength of gelatine gels is, to a fair approximation, proportional to the square of the gelatine concentration.

The effects of varying acidity and pH on the strength of gelatine gels have been investigated by Lampitt and Money (loc. cit.) and TAYLOR [1933]. The former investigators found that the gel strength increased with rise of pH over the range 2.6 to 4.0 but the behaviour was not identical for different acids at corresponding pH values. The latter investigator, however, examined the behaviour of a range of different gelatine samples of different origins and manufacture and found the changes in rigidity to be more complex. In most samples a maximum jelly strength occurred at pH values between 3.7. and 4.3 followed by a sharp drop in strength between 4.4 and 4.9, with a subsequent rise in strength on raising the pH to over 5.

There is little doubt that much further work is required in this field, in which the gelatines should be closely characterized both as regards the removal of impurities such as ash constituents and in respect of knowledge of the molecular weight distribution of the different sized protein molecules present.

The whole question of protein gels has been discussed in detail by FERRY [1948b].

Lampitt and Money (loc. cit.) have investigated the setting behaviour of commercial table jellies prepared according to the directions given on the tablets and the importance of acidity (pH) both in respect of their final gel strength and the time taken to attain this maximum has been demonstrated.

The effects of sucrose and levulose in low concentrations (up to 0.2 molar, or less than 7 %) on the time required for setting of gelatine gels has been reported by FRIEDMAN & SHEARER [1939]. The setting time was found to increase for low concentrations of the sugars (up to 0.02 molar) but decreased rapidly at the higher concentration and was more rapid than in the absence of the sugars.

WARD [1951] has discussed the elastic and plastic properties of gelatine gels in the light of the conditions postulated by TRELOAR [1949] as necessary for rubber-like elasticity and has concluded that a qualitative picture of the behaviour of gelatine in the formation of its gels and their properties under various conditions of time, temperature and stress can be drawn, although much experimental work remains to be done before it can be verified.

2. 3. *Starch Gels & Pastes*

The properties of starch gels and pastes (see Chap. I) will only be considered in connexion with certain miscellaneous food products such as lemon curd, fish and meat pastes, and certain sugar confectioners, products and will not include their discussion in relation to the behaviour of flours in bread and cakes.

SMITH [1943] has reviewed the early results of work on the gelatinization behaviour of starches and has reported further investigations of his own. The gelatinization temperatures for samples of wheat, potato, tapioca, maize, sago and rice starches were determined in each case as the *range* of temperature over which thickening occurred upon slowly heating 5 and 10 % starch-in-water suspensions. The results obtained in this way by Smith confirmed those of CAESAR [1932, 1935] which were obtained with a "consistometer" which measured the power consumed in stirring the paste while it was being heated and also agreed fairly well with figures obtained by REHWALD [1926].

Comparison of starches by a blancmange-making technique was also carried out by Smith (loc. cit.) who found that with the exception of potato, which gave a stronger jelly, the starches with the lower gelatinization temperatures yielded the weaker jellies. Other factors examined were the effect of time of storage on the strength and extent of syneresis of the starch gels (blancmanges), the effect of temperature of mixing on rigidity and syneresis, and the effects produced by prolonged heating of the starch pastes. The main results obtained by Smith in this way, were as follows:

The effect of rising temperature of preparation of starch pastes on the strength of the resulting jellies provided a differentiation of the starches according to (a) maximum strength and (b) the temperature of preparation corresponding to the maximum strength. The strongest jellies obtained were from potato and rice starches, followed by sago and maize starches, then wheat starch and — weakest of all — tapioca. It was stressed however, that tapioca starches may vary very widely.

The temperature of preparation required to give the strongest jelly was also evaluated for each type of starch.

The syneresis of starch pastes and gels decreased as the temperature was raised and with the time of heating. It was possible to regard the syneresis of an unheated mixture of starch and water as approaching 100 % and as the mixture was heated, so more water became bound and was not free to exude.

The maximum rigidity occurred at about that temperature at which the starch cells were so swollen as to rupture, although some rigidity was due to the cell contents alone since all the pastes possessed some rigidity after the starch cells had been broken up. This has been established more definitely by grinding starch with glass without heating. The major effect, however, seemed to be associated with the maximum swelling of the particles and the freshly liberated cell contents.

With some starches there appeared to be a correlation between the phosphate content and the maximum rigidity of the gel but this was not so with other starches.

Five different samples of maize starch, including the yellow type, all behaved very similarly.

Earlier methods employed for measuring the viscosity or "consistency" of starch pastes generally involved the cooking of the starch under standard conditions followed by a single reading of viscosity, usually by measuring the rate of flow of the paste (at one temperature) through a standard-sized orifice. Full details of such measurements are given by KERR [1950]. However, a number of instruments have since been devised which give a complete record of the changes in viscosity (or a closely related but more empirical property termed "consistency") of starch pastes during heating and of these mention may be made of the Caesar consistometer (1932) the Brookfield Viscometer, the Brabender Amylograph, the Corn Industries Viscometer [1947] and the Shirley Consistometer [1946a, 1946b, 1947]. The uses and applications of these instruments in the study of the flow properties of starch pastes have been discussed in detail by SMITH [1952]. The Corn Industries' Viscometer and the Shirley Consistometer are both of particular value in that a reasonably close approximation to particular large scale methods of cooking starch pastes may be simulated under closely controlled conditions so that the continuous recording of flow properties (achieved automatically with the former instrument) may well have direct application to manufacture.

The changes taking place during the heating of aqueous starch pastes containing acids or sugars or both are important in relation to the physical properties of many food products including sauces, piccalilli, custards, blancmanges and lemon curd. SMITH [1949, 1952] has explored the changes taking place in starch pastes maintained at differing pH values and containing sugar in various concentrations, by use of the Shirley Consistometer (loc. cit.).

The presence of acid increases the degree of gelatinization and breakdown of the starch granules and is in opposition to the action of sugar which tends to restrain gelatinization.

At high concentrations of sugar, both WHITTENBERGER & NUTTING [1948] and SMITH [1952], have shown that gelatinization may be completely inhibited. The latter investigator also showed that the changes in gelatinization temperature of potato starch when cooked in sugar syrups of various concentrations are too large to be accounted for by the dilution effect of added dry starch on the starch-water suspension. SMITH [1952] also showed that the final consistency of yellow maize pastes in a syrup of 25 % sucrose concentration was higher than that of the corresponding water paste even when allowance was made for the viscosity of the sucrose syrup. He concluded that this effect must be due to the sugar's inhibiting the completion of the starch gelatinization since the same ratio of starch to water was maintained in both the syrup-paste and the water-paste so that, by its presence alone, the sugar would serve only as a diluent and hence tend to decrease the consistency. Smith has attempted to explain this phenomenon on the basis of a hydrogen bonding mechanism.

The consistency and general physical characteristics of lemon curd are undoubtedly complex and no systematic rheological study of this product appears to have been published. The product as generally prepared is a cooked starch or starch-flour paste containing both acid and sugars together with emulsified fat and a small proportion of egg.

SMITH [1949] has considered the scientific principles underlying the manufacture of lemon curd and has shown how most of the difficulties such as syneresis, fat separation, and "cracking" may be avoided. For the most part the basic factor in lemon curd manufacture would appear to be the correct cooking of the starch paste.

Similarly with products such as sauces and piccalilli liquor, a carefully standardized heating procedure in respect of time and temperature for a given size of batch is essential in order to prevent unsightly liquid separation (syneresis).

Fish and meat pastes are further products whose correct physical condition is largely dependent upon the rheological properties of starch pastes and gels. HARVEY & RAY [1950] have shown how, in respect of meat pastes, such undesirable features as shrinkage of the paste, aqueous separation and separation of fat may all be avoided.

3. Two-Phase Systems

Two-phase systems in food products include solid/liquid systems, ranging from stiff pastes such as fondant cream or icing to very fluid liquid suspensions (e.g. thin sauces), and systems in which the dispersed phase is either liquid (emulsions) or gaseous (foams).

3. 1. *Fondant Cream*

Fondant cream is normally a stiff paste consisting of solid sugar (sucrose) in the form of small crystals dispersed in a syrup saturated with respect to sucrose and containing confectioners' glucose and any invert sugar employed or formed in the course of manufacture. Some air may also be incorporated as very small bubbles.

While no systematic rheological measurements of the "hardness" or other properties such as seepage of liquid under stress appear to have been reported for fondant, nevertheless its structural composition has been examined in detail by HINTON [1925]. This investigator has shown how the proportions of solid and liquid phases may quite simply be calculated from the analytical composition which is readily determined. In addition, the composition of the syrup phase and its viscosity may be evaluated from the same analytical data. The size-distribution of the solid phase has also been shown determinable by Hinton who employed an excess of saturated syrup of approximately the same composition as the syrup phase of the fondant in order to thin out the assemblage of sugar crystals, thus permitting their separate examination under the microscope. In this way it was possible to ensure that no solution or precipitation of further sucrose occurred during the size-distribution measurements.

Increase in the moisture content of fondant results in an increase in the syrup portion at the rate of about 3 % syrup for each 1 % of moisture. The amount of crystalline solid phase diminishes correspondingly.

Increasing the proportion of glucose or invert syrup also increases the amount of the syrup fraction although the effect is not so pronounced as that due to changes in moisture content.

The effect of a rise or fall of temperature on the proportion of syrup is quite small compared with the effects due to alteration of composition.

From direct qualitative examination of a range of fondants of graduated solid-liquid composition it would seem apparent that the major characteristics of hardness and shortness are due in very large degree to the relative proportions of the solid and liquid phases. Other factors such as mean crystal size and size-distribution and the viscosity of the liquid portion do, however, have appreciable effect on such properties as seepage of syrup under pressure.

The structural composition of fondant cream is modified by any subsequent warming and cooking in that the former process results in solution of some of the smaller crystals; so that during the latter (cooling) stage this dissolved sugar will tend largely to be deposited on sugar crystals already present. In all, therefore such treatment results in no change in the total amount of solid phase but does tend to alter its character from one consisting of a large number of small crystals, to one in which fewer but larger crystals are present. In normal, smooth fondant cream, crystals should be less than 15 μ in size and generally many will be much smaller, of the order of $1 - 5\,\mu$ or even less.

If evaporation of moisture takes place from the surface of fondant then occasionally this may bring about movement of the syrup phase from certain crystalline regions to other parts of the fondant and in this way, as shown by HINTON [1929] may cause the formation of white opaque spots in the surface which are particularly noticeable in coloured fondants.

HINTON [1931] has concluded that the desirable characteristics of the arrangement of crystal sizes in a fondant are small maximum size, small average size, and a high degree of diversity of size. He evolved an approximate method for evaluating the comparative magnitudes of these three characteristics. This investigator also showed that there was a steady growth in the mean size over long periods of storage at normal temperatures, probably due to growth of large crystals at the expense of smaller ones. Fluctuation of temperature during the period probably had an accelerating effect on this phenomenon.

He found that the temperature of beating appears to have no well-marked effect on crystal size, but fondant pastes prepared warm, increase in crystal size somewhat more rapidly during the first day of storage. Increased vigour and rapidity of beating did however, result in an appreciably smaller size of crystal.

The proportion of glucose or invert sugar in the paste had no marked effect on crystal size but there was a distinct connexion between the latter and the percentage of water. The greater the proportion of water, the larger was the crystal size. This was attributed, by Hinton, chiefly to viscosity effects and not to the degree of supersaturation.

3. 2. *Grained Honey*

This product is very similar, in its obvious physical characteristics, to fondant cream save that the crystalline solid phase consists of dextrose monohydrate in place of sucrose.

As in fondant, small crystalline size of the solid phase is desirable in grained honey in order to provide smooth eating and spreading qualities and also to avoid the defect known as "frosting" or "dry granulation" which may occur on exposure of the honey to a sharp drop in temperature. If the crystal size is sufficiently small, then any further dextrose thrown out of solution as the crystalline monohydrate will be deposited over such a very large surface of existing crystals that no excessively undue whiteness will be apparent in any part of the container. Should, however, the crystal size be unduly large ("coarse-grained" honey) then a sudden fall in temperature may produce this defect which is manifested by white patches of crystals sharply contrasting with the remainder of the honey.

If the mean crystal size is so small as to make the honey too stiff for normal handling and spreading, then clearly this defect may be rectified by exposure of the honey to a warmer temperature for a short time followed by subsequent return to the normal cooler temperature. As a result the general "fluidity" of the product will be permanently improved since the number of crystals will have been reduced and their size increased. In this way the total solid surface promoting adhesion to the liquid phase, and hence retarding its mobility, will have been reduced. (See also chapter VI).

3. 3. *Suspensions*

Suspensions of finely divided solids in aqueous liquids such as concentrated fruit drinks and thin sauces of the "Worcester" type may probably be treated without serious practical error as two-phase systems, in which the solid phase is present in small amounts compared with the proportion of liquid present, although in some instances the solid phase may consist of more than one type of particle.

The normal flow properties of such suspensions will in general not depart seriously from those of the liquid phase so long as the concentration of dispersed phase is low and flow takes place through orifices which are large compared with the suspended particles.

Although no serious rheological studies of these particular systems appear to have been reported, nevertheless both the concentrated fruit drinks and Worcester type sauces have certain properties which are of rheological interest in that the character of the product may tend to be adversely affected by small forces.

It is desirable in the former class of product that the suspended fruit particles should remain uniformly dispersed throughout the whole of the liquid phase and should not settle out as a sediment when allowed to stand. Conversely the opposite characteristic is required in a Worcester-type sauce where a definite sediment is desired, with the supernatant liquid free from haze arising from some of the particles remaining dispersed in the upper liquid layer.

Adequate dispersion of the solid phase is largely achieved by "homogenization" in which the solid portion is obtained in a very finely divided state but this method alone is probably not a complete answer. The permanent prevention of "clumping" and sedimentation would seem to involve the necessity for provision of adequate repulsion between the dispersed particles in order to prevent their gradual coagulation.

In respect of Worcester-type sauces the author (HARVEY [1946]) has shown that in instances where difficulty in obtaining complete sedimentation has occurred the matter may be corrected by the introduction of very small quantities of suitable colloids containing large negatively charged ions.

3. 4. *Toffee*

As normally prepared by the boiling of fat and syrups together with an emulsifying agent (condensed milk or lecithin) toffee may perhaps be regarded as not strictly a two-phase system.

The hardness of toffee has been measured by GROVER [1943] using a penetrometer devised by TAYLOR [1937]. The instrument consists of a loaded conical plunger attached to a pointer which moves over a fixed scale as the plunger penetrates the toffee. The rate of penetration may be observed with a stop-watch and the penetration in one hour was employed as a basis of comparison. A more convenient figure, which increases numerically as the toffee is made harder, was the "Hardness Index" derived from the penetration P which took place in one hour, viz.:

Hardness Index $= 2 - \log P$.

The Hardness index was found to increase linearly with the temperature to which the toffee was boiled, and changes in the hardness as judged by tasting were more closely represented by changes in the hardness index than by the degree of penetration on any other simple relation.

The hardness of toffee measured in this way by Grover was, however, found to be independant of the fineness of the emulsion. Nevertheless the general "consistency" or "body" of the toffee as assessed by tasting was markedly influenced by the fineness of the emulsion. It would seem therefore, that the penetrometer did not measure all, or quite the same rheological behaviour as that which is made apparent upon eating the toffee.

There is some evidence that toffee (even when milk is absent) may exhibit a limited degree of elasticity upon deformation between certain temperature limits since a change of shape in toffee-pieces may sometimes be observed some while after wrapping has taken place.

3. 5. *Marshmallows*

This product is normally made from gelatine and high boiled sugar syrups suitably beaten together to give adequate aeration before deposition into moulds when "setting" takes place and has been investigated in some detail by TAYLOR [1937, 1946]. In particular, he investigated the viscosity of the hot beaten mixtures, the increase in volume resulting from aeration, the toughness or hardness of the marshmallow after setting, the size and uniformity of the incorporated air bubbles, and the effect of quality of gelatine.

The viscosity was determined by a modification of the falling sphere method while the toughness or hardness was measured by the penetrometer devized by TAYLOR [1937] and referred to in VII, 3. 4.

It was observed that no matter how the process was modified, the concentration of soluble solids had by far the greatest effect on the viscosity. The quantity of gelatine affected the viscosity to only a relatively small extent when the solids were low, but produced a much greater effect, as might be anticipated, with a higher concentration of solids. The time and speed of beating also had a marked effect.

With percentages of gelatine below a critical figure there was a tendency towards a decrease in the extent of the expansion with increasing soluble solids. Above this concentration of gelatine there was, in nearly all instances, an increased expansion with increasing concentration of soluble solids, except when the time of beating was very short.

The concentration of soluble solids had only a relatively small effect on the toughness of the marshmallow and the concentration of gelatine had the most powerful influence on this property. The time and speed of beating and the temperature had slight effects only.

Increase in the concentrations of both soluble solids and percentage of gelatine resulted in smaller bubble size. Although smaller bubbles were obtained in the marshmallows having the higher total solids, the expansion ratio had nevertheless generally increased.

In respect of the effect of the quality of gelatine employed in the preparation of marshmallow it was found that the toughness of the marshmallow was closely related to the jellying strength of the gelatine in aqueous solution. A determination of the foaming ability of gelatine in water alone was not found to be of any marked significance as regards the relative beating powers of gelatines in marshmallow preparation.

4. Multiphase Systems

Under this heading will be considered certain food products whose structural compositions involve more than two phases.

4. 1. *Chocolate*

In the molten state the continuous liquid phase of chocolate will consist of completely melted fat, with, dispersed in it, solid particles of sugar and cacao together with a proportion of crystalline fat if the temperature is not too high. In milk chocolate, of course, there will be present, in addition to the above components, the dispersed non-fatty solids of the milk together with butter fat dissolved in the liquid fat phase. Finally both types of chocolate will contain a small amount of water — usually less than one per cent — whose exact mode of distribution in the chocolate structure does not appear to have been established.

In the "solid" state both types of chocolate will have a continuous, more or less solid, fat phase with the other ingredients uniformly distributed throughout this fatty medium. It should also be mentioned that the presence of entrapped air, as bubbles, may markedly affect the rheological behaviour of chocolate.

CAMPBELL [1923] investigated the viscous behaviour of completely melted plain chocolate, in which all of the fat present was completely liquid, using a modification of the falling sphere method and found that such chocolate exhibited a measure of plasticity. In further work, YOUNG [1934] employed a modification of the Bingham plastometer and determined the yield-value and mobility of a number of samples of completely melted plain chocolates and cacao mass (i.e. chocolate from which the sugar had been omitted). He confirmed Campbell's earlier results and showed that the yield-value was quite small.

In an attempt to devise a suitable instrument for factory control purposes Young (loc. cit.) explored the use of a sinker device operating on the falling sphere principle, and also a flow viscometer of the Redwood type. The former instrument did, however, reveal anomalous behaviour in the melted chocolate in that if a number of successive measurements was carried out by allowing the sinker to fall through the *same* portion of chocolate whilst keeping the latter undisturbed between determinations, then an initial high time of fall was followed by a series of lower but constant readings for subsequent sinkings. If, however, the chocolate was carefully stirred (so as to avoid the inclusion of entrapped air), then a subsequent determination with the sinker device again reproduced the high initial reading.

It would therefore appear that the use of such a sinker device can result in some orientation of the particles of the dispersed phases and so diminish the resistance offered by the chocolate to a body falling through it.

The Redwood type of instrument with a large orifice did, however, yield satisfactory and reproducible results which were but little affected by stirring.

In further studies of the flow properties of chocolate by the capillary tube method YOUNG [1936] investigated the effects of different manufacturing procedures and compositions.

As the yield-value of molten chocolate is comparatively small it was considered sufficient to determine the extrusion rate at one pressure which was sufficiently high to be on the linear portion of the flow-pressure curve, particularly where samples of similar composition, but varying in processing treatment, were under consideration. Obtained in this way, the "viscosity" was found to be influenced by processing procedures, as follows.

The viscosity of the cacao liquor obtained from the roasted beans decreased with increased degree of roasting. Only part of this decrease in viscosity could be attributed to the extra fat made available from the higher degree of roasting, since the viscosity was also diminished by steam treatment of the beans whereby the available fat remained unaltered.

Refining increased the viscosity of chocolate in the manner to be expected from the decreased particle size of the dispersed solid components.

The viscosity of chocolate free from air bubbles was found to decrease with rise of temperature in the same manner as for cacao butter alone.

The conching [1] of plain chocolate showed a decrease of viscosity with time of conching but on long conching at a high temperature there was a very slight increase in viscosity, due possibly to a slight decrease in size of the sugar particles.

With some milk chocolates there was found to be an appreciable increase in viscosity after 18 hours conching at 55° C, before which there had been a decrease. Milk chocolates conched at 55° C, increased in viscosity on storing at 55 — 60° C.

The reductions in viscosity produced by lecithin and cacao butter were compared by Young (ibid) and found to depend on the viscosity and the proportion of lecithin added. In favourable circumstances the effect of lecithin was found to be as great as that of from 10 to 30 times its weight of cacao butter. Full plasticity data were evaluated for the action of lecithin when it was shown that the mobility was increased and the yield-value decreased.

The effect of addition of lecithin in reducing the viscosity of chocolate, was considered to be due probably to a reduction in friction between the sugar particles and the liquid fat medium. This was probably achieved by orientation of the lecithin at the surface of the sugar particles so that the non-polar portions of the lecithin molecules were in contact with the continuous oil phase.

STAINSBY [1941] has investigated more fully the anomalous behaviour shown, by Young (loc. cit.), to occur when certain milk chocolates are subjected to heat treatment. He found that for milk chocolates made with spray-dried full cream and separated powders, the viscosity changes on heating the chocolates at various temperatures indicated that the full cream powders gave chocolates less stable to heat. The trouble was found to be largely avoidable if the milk powders were given a suitable preheating treatment before incorporating them with the other chocolate ingredients. The addition of small quantities of certain salts was also found to prevent any increase in viscosity upon heating milk chocolate. In one case an actual decrease of viscosity was produced by this treatment.

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[1] "Both plain and milk chocolate are refined in a 'conche' in which heavy rollers move to and fro over a granite base". Chambers' Encyclopaedia, 1950 edn.
Editor.

Grover & Wertheim [1948] have described a new type of capillary viscometer suitable for measuring the flow properties of liquids which enable viscosity over a wide range of shearing forces to be ascertained by a single test. The liquid to be studied is contained in a vessel open to the air but connected by a short capillary tube with a partially evacuated vessel of known volume connected with an air-pressure gauge. The rate of flow of the liquid from the open container into the partially evacuated vessel of known volume can be calculated from the fall in pressure indicated by the pressure gauge. There is a special arrangement provided for returning the liquid from the partially evacuated vessel into the open container.

Hallas & Steiner [1950] have employed a modification of this viscometer to measure the flow properties of molten chocolate under varying shearing stresses. The instrument was found to be particularly suited to the examination of flow properties at or near the graining temperature (i.e. when crystallization of the cacao butter commences) and also while graining is in progress. The instrument also readily permits of observations of any change in rate of flow with time at constant temperature, since readings can easily be repeated at intervals.

4. 2. *Marzipan*

As normally prepared from almonds and sugar the structural composition of marzipan is of considerable complexity. The product consists principally of small solid particles dispersed uniformly throughout a continuous liquid medium. This latter phase is an aqueous syrup containing, dissolved in it, the soluble constituents of the almonds, together with all the sugar required to effect saturation of the syrup. The solid portion consists of the excess undissolved sugar present, together with the insoluble solid constituents of the nut. Any almond oil liberated from the oil cells during manufacture is also distributed throughout the marzipan paste and the mode of distribution, whether as isolated small droplets or larger continuous regions, may be expected to affect the physical characteristics of the product. Oil retained within the nut cells may, however, contribute to the composition of the solid portion.

The proportions of both the liquid and solid components will be largely governed by the original proportions of nuts and sugar employed, together with the final water content of the batch. The extent to which oil is liberated from the nut cells will depend on the technique of manufacture.

Marzipan is characterized by well-known plastic properties which permit ready moulding into any required shapes. It may also be readily spread upon and made to adhere to other surfaces, while suitable treatment and manipulation may provide a glossy finish due to the formation of a continuous oil film.

In its major aspects much of this physical behaviour will probably be governed by the relative proportions of the solid and liquid phases, as with fondant cream.

Systematic rheological measurements of the behaviour of marzipan under deformation do not appear to have been reported but the understanding and practical utilization of such behaviour will certainly call for a knowledge of the structural composition of marzipan.

Jones [1951] has shown how the measurement of refractive index of marzipan coupled with one other simple analytical determination (such as the water content) or knowledge of the propertions of almond to sugar may provide such structural and compositional information. By means of these simple determinations, Jones has shown that the proportions of solid and liquid phases and the full composition of each may be evaluated.

CHAPTER VIII

PSYCHO-RHEOLOGY OF FOODSTUFFS

BY

R. HARPER

PSYCHOLOGY DEPT. THE UNIVERSITY, LEEDS, ENGLAND *

0. Introduction

Perhaps the term psycho-rheology needs some explanation. In this chapter, studies primarily involving the assessment of human reactions to the rheological behaviour of materials with special reference to those which are judged, literally, by handling will be reviewed. As this field of study has been developed systematically only over a short period of time by a small number of workers, it is justifiable, and indeed necessary, to include work that has not been carried out on foodstuffs, providing such studies contribute to fundamental methods of analysis. Although there is a need for further development of effective rheological tests on foodstuffs, in most instances it is some human response which is of final importance. That the subjective human judgment should be dispensed with is both unlikely and undesirable. This is being increasingly realized in the Food Industries and means of standardizing and refining the technique of assessing or scoring food products are to be welcomed. Although in the later parts of this chapter some aspects of and observations on the assessment of non-rheological properties or qualities of foodstuffs will be included, clearly, a general discussion on this important topic would be out of place here (see HARPER [1949c, 1950b]).

At least in the present state of the development of methods, the relationships between objective measurements and subjective assessments on foodstuffs are imperfect. These imperfections extend, it is believed, beyond the mere errors of observation. Thus, prediction of subjective characteristics from objective measurements can only be partially effective. This may be in part due to important differences between the numerical aspects of objective measurements and the

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* Formerly of the National Institute for Research in Dairying, The University, Reading, England.

numbers used to characterize subjective impressions. In physics Bridgman [1928] has correctly emphasized the need for a clear understanding of the *operations* of measurement, the way these affect our subsequent processes of thought and the concepts used to describe a given field of relationships. In psycho-rheology, particularly where quantitative expressions are used, it is just as necessary to be aware of the consequences of the *processes of measurement.* Here too, it is impossible to separate entirely a given observation or concept from the methods whereby it is derived. In short, there are probably no purely objective measurements which are not to some degree dependent on the particular method selected for carrying out the implied operations.

Developments in the present field will be reviewed mainly in chronological order except where earlier studies are connected with a later, major work. Thus, much of the first part will be concerned with a number of mainly qualitative or descriptive studies carried out at a time when the rheological treatment of the materials concerned, under conditions of everyday use, was not very advanced. However, physics and rheology have all passed through important purely descriptive phases. Systematic and reliable description is a pre-requisite of any useful numerical treatment. Kelvin's much quoted dictum [1]) is only partially true, for the purely numerical forms of description can only remain effective where, by agreement or convention, a relatively narrow and closed field of human knowledge is considered. When broader relationships are being studied, some form of numerical treatment and an assessment of the statistical significance of the observed effects are equally desirable.

1. Early Investigations, Mainly Qualitative

Certain qualitative investigations into the human response to rheological stimuli and the integrated nature of the perceptions or experiences, based upon patterns of rheological stimuli and their time variations, will be reviewed. These may not be directly concerned with foodstuffs, but the fundamental relevance of the underlying principles, justifies the inclusion of a brief resumé of the work concerned.

One of the earliest systematic investigations reported was that of

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[1]) "......often I say that when you can measure what you are speaking about and express it in numbers you know something about it; but when you cannot measure it, when you cannot express it in numbers, your knowledge is of a meagre unsatisfactory kind......." (Kelvin (Sir W. Thomson) [1891]).

SULLIVAN [1923] into the perception of what was termed liquidity, semi-liquidity and solidity. The work was carried out at a time when the definition and description of rheological conditions were inadequately developed, but in essentials the meaning of the terms used is self evident. The large class of experiences included in the term "liquidity" were considered to be true blends or fusions, but the equally large number of experiences included in the term "solidity" such as dry, soft, hard, etc., were rather cutaneous patterns or mosaics. By changing the temperature of water, in which a blindfold subject's finger was immersed, a whole series of experiences ranging through the liquid, semi-liquid and solid impressions were aroused, thus: 0° C (Mushy) 15° C (Gelatinous) 20° C (Wet) 38° C (Oily) 42° C (Greasy). This work shows the complex nature of experiences which, to the psychologically untrained, might be regarded as determined by a small number of commensurate physical properties.

ZIGLER [1923], and MEENES & ZIGLER [1923] reported studies of the perception of roughness, smoothness, clamminess and stickiness. The importance of movement and of the pattern of stimulation is stressed. It was found possible to synthesize the experience of stickiness by allowing the skin to be pulled and released by a set of small hooks. The essential subjective characteristics of roughness and smoothness were defined, and although movement was an essential part of the stimuli giving rise to such experiences, it was felt to belong to the stimulus rather than to the characteristics of roughness or smoothness. In the absence of movement, the experiences were labelled "unevenness" and "evenness".

Working on the judgment of the softness of wool tops BINNS [1936] has demonstrated the importance of visual clues in judgments based upon rheological stimuli. The data reported suggest that the use of sight alone was very much more accurate for the expert, than judging by touch alone. When the experts were blindfolded, three schoolgirls under similar conditions were quite as good as the experts, who were judging by touch alone. However, the general disturbance caused to the experts by the mere fact of being blindfolded and subjected to these tests cannot readily be assessed. In such work the mental state of the subject and the conditions of testing play a very important part in the results obtained. Such investigations should, then, be carried out under carefully controlled conditions approximating as closely as possible to the normal conditions of work. Incentives, and the subject's attitude and interests are among the influences which should be described and controlled to the fullest possible extent.

Katz & Stephenson [1937] compared the subjective impression derived from pulling an elastic spring, with that of lifting the same dead weight. The impression was considerably greater for lifting the weight than for exerting the same force on the elastic spring. The former must be supported almost instantaneously; the latter builds up progressively from zero to the selected value. Thus the time characteristics of the stimuli play an important part in determining the apparent intensity of the subjective experience.

Grindley [1936a, b] made investigations of the effect of varying the rate of application of the stimulus, on the "thresholds" 1) for touch, pressure and pain. The effect on those for pressure and touch were pronounced; when the rate of application of pressure was changed from 50 g/sec. to 2000 g/sec. as much as a tenfold decrease in threshold was observed. This has very direct bearing on the discrimination of various rheological properties, although the forces are *actively* applied by the subject rather than applied *passively* to him. It will not be surprising to find that in comparing certain materials, the time characteristics of the stress/strain relations play an important part. In most forms of human discrimination, processes or changes which occur very rapidly or very slowly may not be experienced immediately. Over a certain range rates of change, or possibly some "intermediate" function, may be important (see VII, 2. 2).

2. Fundamental Quantitative Studies

2. 1. *Comparison of Similar Materials*

Scott Blair & Coppen [1939] reported fundamental experiments in which they determined the "differential threshold" for the viscosities and compression moduli of selected materials. In this, they first introduced a generalization of the equations for the behaviour of Newtonian and Hookean prototype materials, suggesting for complex materials, the form:

$$\tau = \psi \varepsilon t^{-k} \tag{1}$$

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1) Very briefly, the "threshold" is a measure of the intensity of the stimulus required to produce a specified response on a defined number of occasions of judgment.

See Harper [1950a] for more detailed information.

where

τ is the shearing stress.

ε is the shearing strain.

ψ represents the "firmness" of the material, the dimensions of ψ being dependent on the value of k.

k is a time exponent.

This, as was afterwards realized, is a special case of the equation proposed by NUTTING [1921a, b]. The bent lever constant stress rheometer was used to measure ψ and k for a number of complex materials.

Scott Blair and Coppen suggested that any exceptional skill which the expert might claim in judging the rheological properties of materials and in making use of such judgments must be ascribed to one or more of the following conditions:

(1) The ability to distinguish small differences in rheological properties, of which viscosity and compression or shear-modulus are typical.

(2) Recognition of rheological conditions previously associated with desirable or undesirable situations.

(3) Technical knowledge enabling the information derived from (1) and (2) to be effectively utilized.

The first experiments were concerned with the differential threshold for viscosity and for this purpose a series of samples of almost Newtonian, Californian Bitumen (subsequently termed, simply, bitumen) was selected, diluted as required with small amounts of Golden Flux Oil. The viscosities were determined by the method of rheograms (SCHOFIELD & SCOTT BLAIR [1933], see II, 2), the selected samples differing by 0, 7.5, 15, 22.5 and 30 %. These were presented to the subject (observer), in pairs, in a random order. Handling the samples was carried out, under water, in any way the subject chose. Temperature control was necessary owing to the high viscosity-temperature coefficient of the material and the water also served to prevent the fingers sticking to the bitumen. Judgments were made as to which sample of each pair was the firmer.

The thirteen subjects who took part fell into 6 main groups so that both individual and group differences could be considered. The main conclusions were that there was no significant [1] difference between the individuals in their ability to distinguish differences in viscosity of the samples of true fluid bitumen. Subjects with experience in routine chemical analysis showed a significant advantage. Age and general education appeared to be disadvantageous. The cheese technologists, as a group, were not significantly different from the rest; age and general education appeared to be disadvantageous. As subjects, the experimenters themselves were in no way superior, although they alone understood the purpose and planning of the experiment. When the data for all subjects were pooled, the proportion of correct judgments (using the objective measurements as a standard) reached a level of 80 % for viscosity differences of 30 %.

The experiments on rubber were carried out as follows. A number of samples 2.5 cm in height and 2 cm in diameter were prepared specially for the investigation. As the differences required were rather small, the selection of specific samples was essentially by trial and error. The numbers of samples in various groups and the differences in compression moduli between the groups were not equal. A simple compression rheometer was built allowing the samples to be compressed under a load of 20 lb (9.08 Kg), and the deformation measured. Relative rather than absolute figures were required.

Ten subjects were used this time, and in each test fifteen pairs of samples were presented for comparison by compression between finger and thumb, in random order. In the main experiment with rubber, handling under water was not required. Unlike the viscosity experiment, highly significant differences were observed between individual subjects in their ability to judge differences in the compression moduli of the rubber samples. Inter-group differences were also observed. The routine chemical analysts and the younger or less educated subjects were superior to the rest. Two cheese technologists who were well above average age were significantly *inferior*. When the results were pooled the proportion of correct judgments reached a level 80 % for differences in moduli of 10 %.

The difference between discrimination in the two cases is shown effectively in Fig. 1 in which the objective criterion is expressed in terms of the logarithm of the percentage difference (Δ) between the samples compared. It was suggested that the threefold difference between the two forms of discrimination may be attributed to the fact that viscous materials can *only* be judged dynamically ¹) whereas the rubber samples may be judged statically. (In addition, since the elastic materials recover almost completely on releasing the pressure a repeat, or confirmatory test may be made under similar conditions to the first test. With materials which do not recover this is not possible).

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[1] The term significant is used in the special statistical sense.

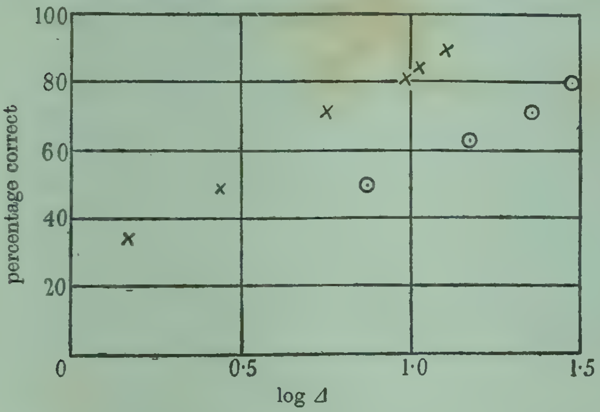

FIG. 1. Discrimination of differences in compression moduli ×, and viscosity ⊙. (See text for details.) [*from Scott Blair and Coppen, Proc. roy. Soc. B*, 128, 109 (1939) p. 123].

SCOTT BLAIR & COPPEN [1940a] reported further experiments using bitumen, rubber and a complex plastic material (comparable with cheese in rheological properties) made by mixing plasticine, vaseline and rubber solution and evaporating the solvent. A preliminary experiment indicated that when standard samples of bitumen and vulcanized rubber were compared with one another, the judgment of relative firmness was greatly dependent upon the time of compression, whereas the effect of changes in pressure was small. The main work reported was concerned with the effect of training and experience on the judgment of the firmness of samples of complex materials which differed in springiness ²) in addition to the amount of deformation under specified conditions. Nineteen subjects took part in the experiment, carrying out the test between 24 and 26 times. In this, they were required to place eight samples in order of firmness. Apart from the experimenters, who also acted as subjects, neither the purpose of the experiment nor each individual's progress were discussed (in any psychological study knowledge of results may be an important

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¹) The term "kinetically" was subsequently suggested by Scott Blair as being more correct.

²) Later work has suggested that there may be differences of opinion in the definition of springiness.

condition, as indicated by an investigation of muscular coordination by ELLWELL & GRINDLEY [1938]).

Objective measurements were made using the same simple instrument as in the previous study (SCOTT BLAIR & COPPEN [1939]). The samples were compressed for 2 sec. and then released, deformations at the end of the loading period and after 1 minute recovery being recorded. In addition, a repeat test using 10 sec. compression was made. The ratio of the 2 sec. to the 10 sec. deformation was taken as a rough measure of strain hardening.

The main purpose of the present study was to assess the development of the subjective discrimination, and only secondarily to relate subjective judgments to objective measurements. The experimental data were divided into two equal halves and the variance of the rankings for each subject determined for each section, working about the means for each half, separately. The variances were divided by the corresponding number of placings and square roots taken. Denoting these by σ_1 and σ_2 they might be regarded as an index of self-consistency for each half and a learning factor Λ defined as σ_1/σ_2 was calculated. A partial analysis of variance was carried out on these indices.

Again the routine chemical analysts showed themselves superior in self-consistency to the rest of the subjects, in spite of their lack of experience in this type of work. The group of five cheese technologists was significantly *inferior* to the rest in the learning factor. As individuals, during the course of the experiment, the technologists tended to become less, while the remaining subjects tended to become more consistent in their judgments. An investigation into the consistency of judgment of these two groups as a whole, rather than as individuals, showed that both groups tended to become less consistent, as the experiment proceeded, and that the cheese technologists showed greater individuality, especially in the first half of the experiment. Although it is difficult to state conclusively the reasons for these differences, the authors suggested that mental attitude played an important part. The fact that the routine chemical analysts were used to carrying out lengthy tasks without understanding their full significance and importance has already been mentioned. Further, the cheese technologists' judgments in their own sphere are normally accepted without question and are given for immediate practical use. As the experiments proceeded boredom might well have contributed to the deterioration of their performance.

Coppen [1942] extended the work on the comparison of qualitatively similar materials to include an estimated "threshold" for the complex synthetic materials used in the experiment just described. A modification of the ranking method was used in which it was assumed that, for himself, each subject's judgments were correct. This assumption was necessary to allow for idiosyncrasies in judgment arising out of individual variations in the time of compression or in the pressure exerted. On the basis of the average ranking by each subject of the "firmness" of 8 different samples of the present materials, the appropriate objective difference between the various sample pairs was estimated using, in addition, the total deformation of the hardest and softest samples in two seconds. The logarithm of this difference was plotted against the percentage of correct judgments, as assessed from samples whose position was confused with more than one other (samples confused only with each other would give essentially the mean rank of the samples concerned and this was used previously in calculating the appropriate objective differences). Fig. 2 gives the results of this experiment in which the average sensitivity of judgment for the complex materials was almost indistinguishable from that for

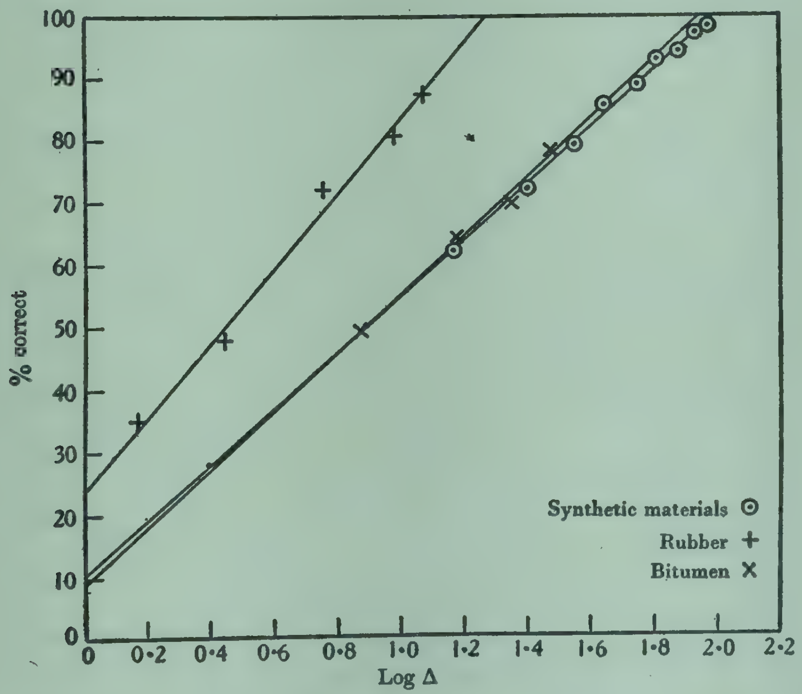


Fig. 2. Comparison of the discrimination of differences between samples of qualitatively similar materials.
[*from Coppen, Brit. J. Psychol.* 32, 231 (1942) p. 238].

bitumen. Comparisons were also made in this experiment between the different groups of subjects. The superiority of the routine chemical analysts, in the proportion of correct judgments made, was again demonstrated. Differences in the slope of the fitted line (sensitivity) were not marked.

Comparable calculations were made, representing the judgments of one cheesemaker, who had taken part in the other experiments, on the "firmness" of cheese curd at pitching (see V, 2 for a description of this stage). Using eleven categories of judgment, the rank order of the cheese made on any one day were determined. The percentage difference in "firmness" (objective) was calculated from measurements using a test described elsewhere by SCOTT BLAIR & COPPEN [1940b], (see V, 3) and a "threshold curve" was plotted. When the cheese technologist was assessing her own familiar material, her performance was above the average for bitumen and for the complex plastics. Although less than the average for rubber, for differences exceeding 10 % her performance with the cheese curd was superior to her own with the mechanically simpler, vulcanized rubber. In cheese curd, "springiness" and "firmness" are correlated, but not in the synthetic materials. Thus additional clues were available for differentiating the firmness of cheese curd. Further information may be obtained from particle size in the cheese curd, fine cut curds being somewhat firmer objectively. On the other hand, the objective measurements on the cheese are likely to be more variable than measurements on the other materials. This would lead to a reduction in the apparent sensitivity.

The present series of studies had to be discontinued owing to the war but were resumed in 1946. HARPER [1949a] reported further work on the subjective judgment of the "firmness" of vulcanized rubber. Objective measurements took the form of the deformation of the cylindrical samples between parallel plates on a simple, constant load rheometer. The value of the deformation Δl divided by the *final* height (l) was calculated, for LETHERSICH [1944] has shown that for materials whose Poisson Ratio is $\frac{1}{2}$, constant load measurements are *mathematically equivalent* to constant stress measurements if in calculating the strains, the final height in the former is substituted for the initial height in the latter. In order to make the functional relationship between the measurements and the frequency of judgments of a specified type as near symmetrical as possible, a logarithmic criterion was used. Thus if $R_a = (\Delta l/l)_a$ and $R_x = (\Delta l/l)_x$ then, on the basis of previous work, the appropriate objective difference between samples a and x was defined as $R_{ax} = \log (R_a/R_x)$. Data obtained by pooling the repeated judgments of 9 individuals on twelve separate pairs of samples were systematically analyzed using the technique of Probit Analysis (FINNEY [1947]). The points of special interest were:

(1) More than one form of physical behaviour may be involved in the experience called "firmness".

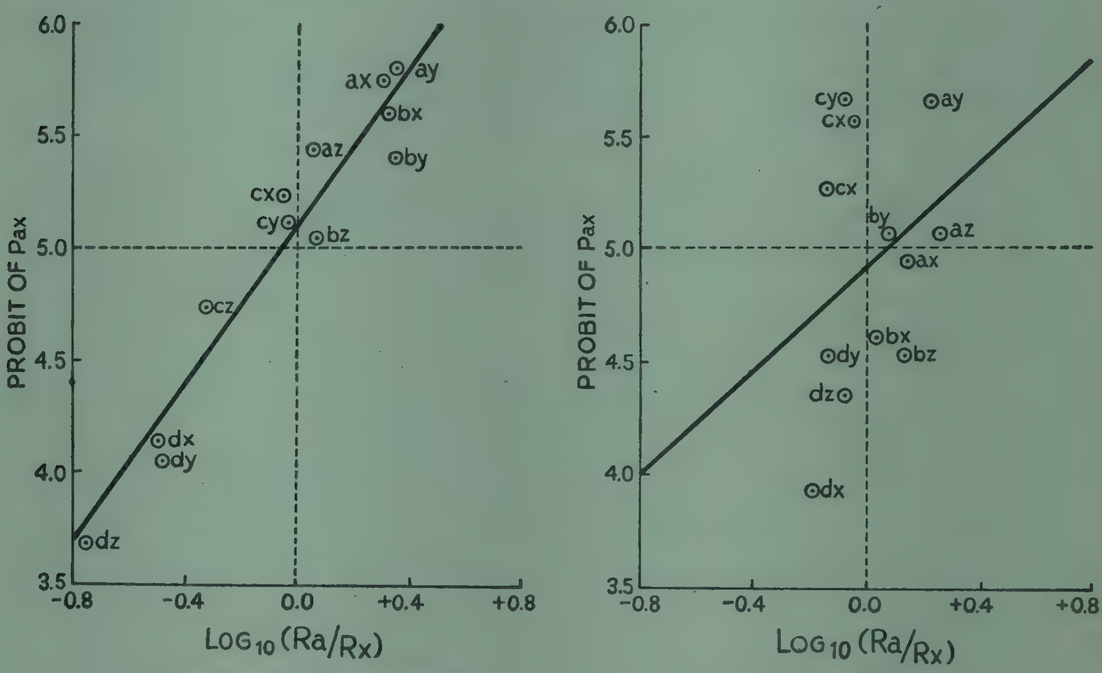
(2) A systematic deviation was noted between the point of equality of two samples as defined by objective measurement and equality subjectively defined (corresponding to 50 % judgments "firmer"). This was interpreted as indicating a higher sensitivity in differentiating soft samples as compared with that involved in differentiating firm ones.

(3) Pronounced individual differences in sensitivity and in the effect of practice were indicated. After several months' regular practice the experimenter himself attained a degree of sensitivity four times the general average.

(4) At this stage, sensitivity was comparable with the accuracy (reproducibility) of the objective measurements.

The results of this experiment are shown graphically in Fig. 3.

Further aspects of the work of which the data reported in the previous paper formed a part have been described. HARPER [1950c] studied the discrimination of the firmness of vulcanized rubber as shown by a number of individuals over a period of about six months. The characteristics and general level of sensitivity varied widely. Some subjects showed a progressive and sustained improvement in performance, probably related to their interest in the task and engendered by their own attitude. Others showed a decline in performance after the first few tests. Still others oscillated widely from one occasion to another so that no trend was evident. Such oscillation was believed to reflect the temperamental characteristics of the subjects concerned. The continuous record of performance, expressing sensitivity, denoted by K, in arbitrary units is given in Fig. 4. In the same paper some interesting group differences in sensitivity were reported. In particular, Dairying Instructresses and students of Dairying were significantly *better* than other groups. This is at variance with the previous observations by Scott Blair and Coppen on cheese technologists (see VIII, 2.1). The difference is believed to have arisen owing to the greatly shortened length of the present tests, as compared with those used previously. It was suggested that under such conditions of testing there is some transfer of skill and interest from the everyday occupation of those connected with dairying, but that in view of the apparent purposelessness of these highly academic tests, performance is likely rapidly to decline. On the questions of transfer of skill it is of interest to note that the highest recorded level of discrimination was that of a blind masseur, although emotional disturbance prevented him from carrying out a complete test.



A MODERATE DIFFERENCES IN OBJECTIVE CRITERION

B SMALL DIFFERENCES IN OBJECTIVE CRITERION

FIG. 3. The relationship between objective measurements and the judgment of relative firmness of samples of vulcanized rubber.
[*from Harper, Psychological and Psychophysical Studies of Craftsmanship in Dairying* p. 27].

Other aspects of the present work will be described in a Monograph entitled "Psychological and Psychophysical Aspects of Craftsmanship in Dairying" (HARPER [1952]). This is an integrating contribution to the present field of study, and may profitably be consulted. The most important conclusions, not reported elsewhere, will be summarized.

Using one small group of subjects it was shown that the average discrimination of the "firmness" of vulcanized rubber was indis-

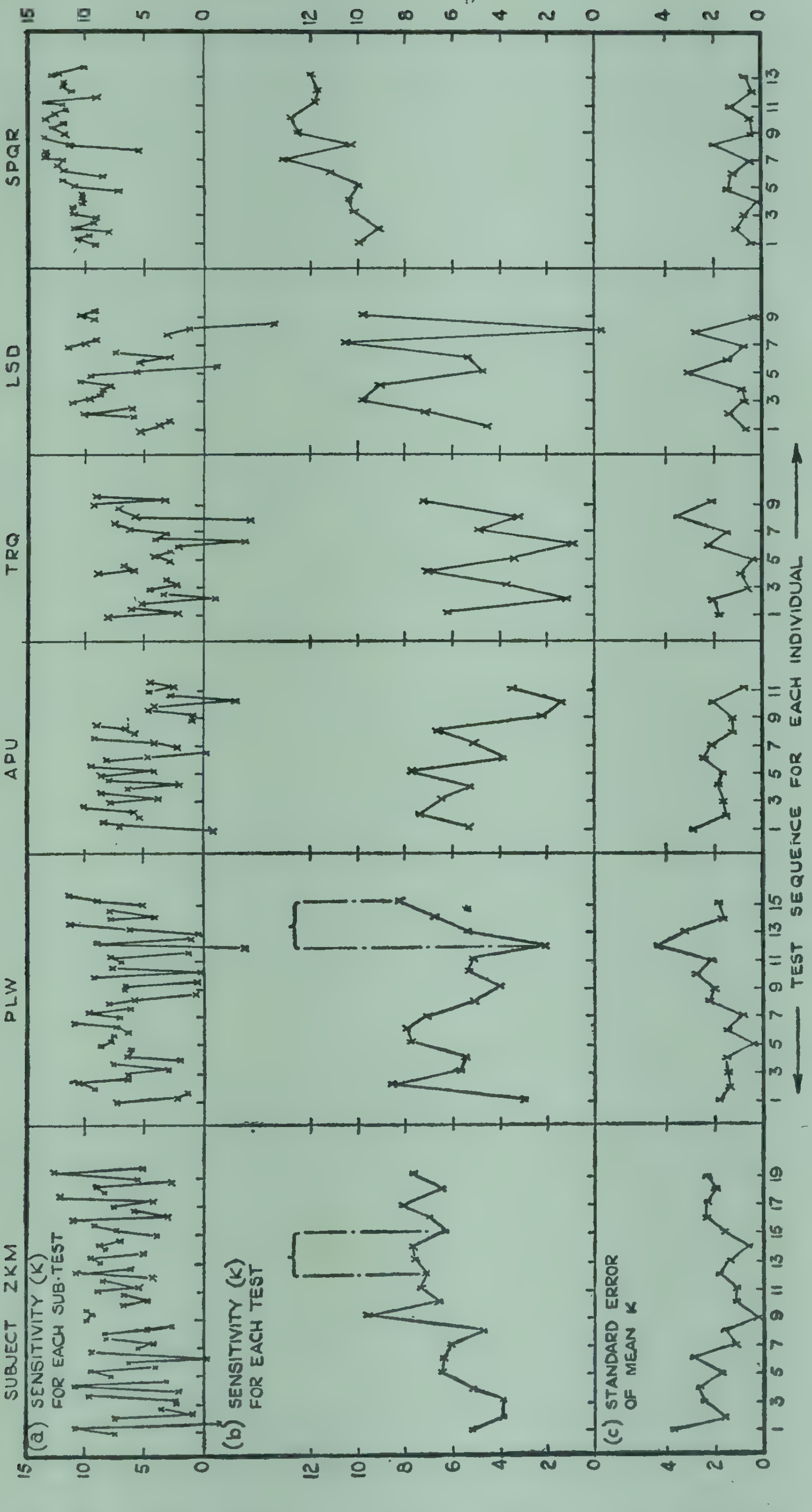


FIG. 4. The development of the discrimination of the firmness of vulcanized rubber. [*from Harper, Occupational Psychol.* 24, 230 (1950) p. 234].

tinguishable, whether simultaneous compressions using both hands or rapid, successive comparisons, using one hand only, were made. Whether the same conclusion would be drawn with two separate, matched groups for each procedure, cannot be answered.

In experiments carried out over a prolonged period, progressive changes occur in the test material (vulcanized rubber). In the investigations discussed these changes resulted in a progressive increase in the difficulty of discriminating, and although a numerical correction may be made for this, the more difficult task is likely to be approached with less confidence than the easier one, so that a simple correction may be inadequate.

It was shown that the experimenter's judgment in his initial test was far more discriminating than that of other persons tested at the same time. In the course of time his sensitivity was approximately doubled, at which stage the errors in judgment were not more than twice the errors (variability) of the objective measurements; the uncertainty of judgment having been estimated on the assumption that the objective measurements were without error. It was also shown to be possible to train an individual in this form of discrimination. A fourfold improvement took place in a series of 31 tests over a period of 10 weeks. This achievement was accomplished by providing adequate incentives, including knowledge of results. In spite of this, pronounced fluctuations in general level of performance from one day to another, believed to be related to preoccupation, worry and other psychological conditions, were noted. The record concerned is reproduced in Fig. 5.

In addition to oscillation from one day to another, evidence was presented to suggest that the performance during a single test might fluctuate. The extent of this oscillation may be an expression of temperamental predispositions, thus raising the question as to whether certain persons are unsuitable for carrying out such operations. The question must at present be regarded as an open one, on which reliable information is urgently needed.

Where any important subjective criterion is related in a complex way to several underlying objective measurements, the use of a single objective measurement will be inadequate to "explain" (i.e. account for) all the observed differences in judgment. Under these conditions the data are said to be *heterogeneous* — in a statistical sense. This question is discussed at some length, for the smaller the differences in any one of the objective criteria are made between the samples compared, the more important will differences in the remaining criteria become. This makes the establishment of simple, universal relationships between the instrumental measurements and the subjective

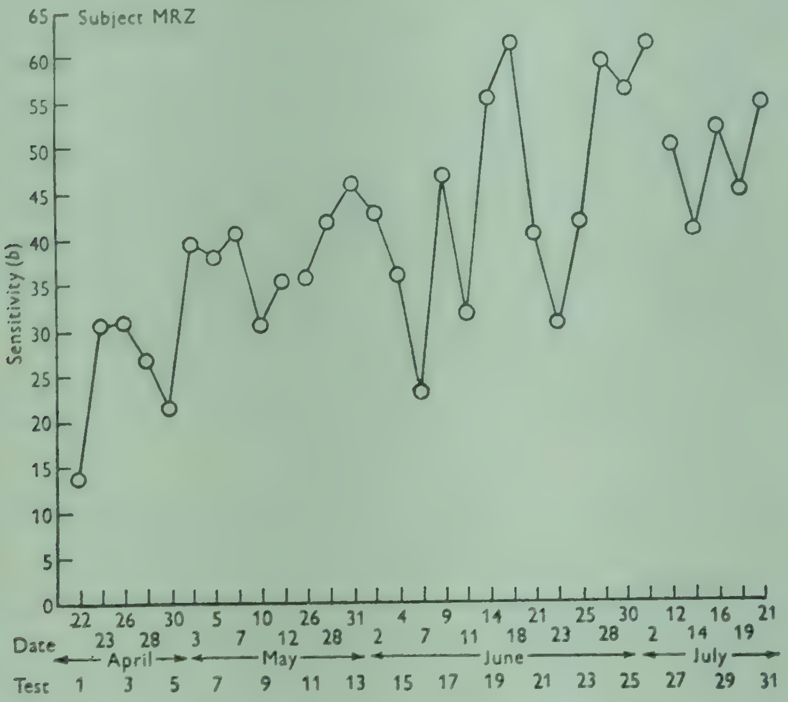


FIG. 5. Detailed study of the development of the discrimination of the firmness of vulcanized rubber. One individual, over a period of 2½ months. Sensitivity (b) estimated by means of Probit Analysis.
[*from Harper*, (1952) p. 48].

judgments all the more difficult to formulate. Both the subjective judgment and the objective measurement may each have its own special function and it may be impossible effectively to predict the subjective judgment from the available instrumental measurements, (or vice versa).

In many instances, including the description and assessment of foodstuffs, it is precisely these subjective characteristics which are most important. Their prediction is the intended function of the objective measurements. Or, preferably, the objective measurement *should* be a more efficient indication of what is desired. The evidence seems to point to the fact that the subjective assessments are indispensable and that it would be profitable to devote both effort and resources to refining and standardizing the process of subjective assessment, especially in numerical terms. Included in this process of standardization would be the provision of individual cubicles, with controlled conditions of ventilation and illumination, where the subjects or judges may be comfortably seated while independently recording their quantitative judgments, amplified by comments [1]).

2. 2. *Comparison of Dissimilar Materials*

Scott Blair & Coppen [1942] reported the first of a series of studies in which the materials compared by handling were qualitatively different (i.e. the physical properties underlying the judgment of relative "firmness" were dimensionally disparate). The materials compared were such that their rheological behaviour could adequately be described in terms of the equation introduced earlier, namely

$$\psi = \tau\, \varepsilon^{-1}\, t^{k}$$

The authors "did not, as a matter of fact, anticipate that log ψ and k would in general prove to be constants of materials, but expressed only a hope that they might both serve as simpler variables than were viscosity and the elastic moduli as well as being more effectively related to the subjective conception of firmness". However log ψ and k for a wide variety of materials were reported as remarkably independent of strain and, except in a few cases, of stress.

The first experiment reported in this series involved the comparison of a number of rubber cylinders with bitumen cylinders. These were all 2.5 cm in height and 2.0 cm in diameter. Ten subjects took part in the investigation. After a few preliminary tests each subject was given in one hand, one of a number of replicate bitumen cylinders, and in the other, one of four different rubber cylinders and asked to compress these simultaneously, between finger and thumb. The compressions were made in time to a metronome. Before making a judgment as to which sample was the firmer the subject changed hands and was given a replicate, undeformed sample of bitumen. In view of the temperature coefficient of the viscosity of the bitumen and also its stickiness, the samples were handled under water at an approximately constant temperature. The bitumen had a viscosity of 1.13 × 10^7 c.g.s. units; the shear moduli of the rubbers were 0.48, 0.42, 0.33 and 0.25 × 10^7 c.g.s. units. Four times of compression were used, 0.5, 1.0, 2.0 and 4.0 sec. The orders of presentation for time, modulus of rubber, and the initial hand into which the rubber sample was placed, were carefully randomized. Altogether a single session involved 32 judgments per subject and lasted approximately 20—30 min. Every subject carried out 8 tests on separate days.

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[1]) Cf. Hopkins [1949], of the National Research Council of Canada.

In these experiments, the time of compression was an explicit variable. The data obtained gave a unique curve when the percentage of "bitumen softer" answers was plotted against the logarithm of the product of the shear modulus of the rubber sample (G) and the time allowed for compression (t_c), and, except for the longest time-interval, the relationship was remarkably linear (see Fig. 6). The intercept on the abscissa corresponding to $p = 50$ gives what is usually termed the "point of subjective equality". The dotted vertical line indicates the position corresponding to the viscosity of the comparison standard, (i.e. log η). The pronounced deviation of the point of subjective equality from this line may be interpreted as follows. A judgment of equal firmness between rubber and bitumen samples having *numerically equal* shear moduli and viscosity (the latter based upon the usual time unit of 1 sec.) would occur when the subjective compression time is a fraction only (in this case 1/3) of the time used in the definition and measurement of the viscosity.

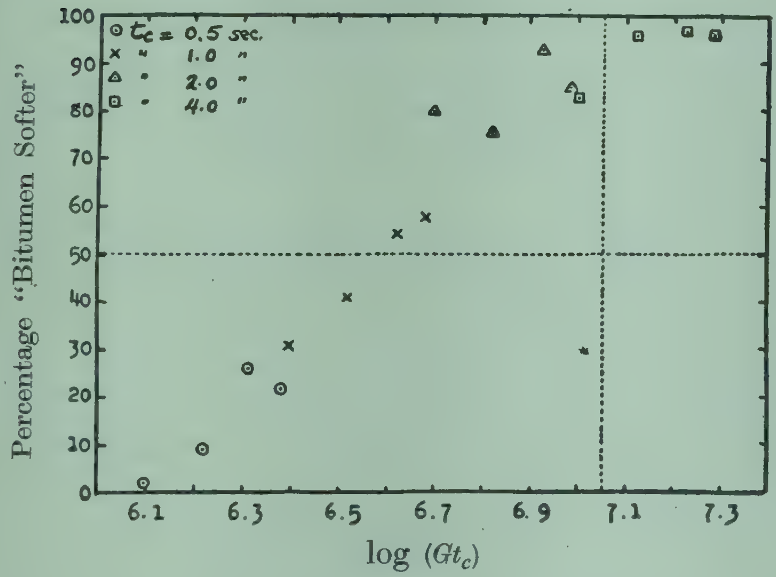

FIG. 6. Data from the simultaneous comparison of a number of rubber samples with a standard bitumen sample.
[*from Scott Blair and Coppen. Amer. J. Psychol.* **55**, 215 (1942) p. 220].

Other observations included the following. In a subsidiary experiment in which the bitumen samples were given a series of compressions, including changing hands, a similar relation between p and log (Gt_c) was observed, but a slight over-compensation for the excessive deformation of the bitumen samples was suggested. Another experiment, using non-simultaneous compression (one hand only), introduced a new effect: the separate portions of the curve were no longer independent of time. A time-dependent shift was noted. The main effect of the displacement of the "point of subjective equality" from that expected on purely objective considerations was again confirmed.

In the ensuing discussion emphasis was placed upon what has been called the α-term, [1]) the fraction by which the objective compression period (upon which the measurements are based) must be multiplied in order to give the required subjective compression period, so that the *numerical* equality of the objective measurements might agree with subjective judgment of equality. For subjective purposes it was suggested that one might define the appropriate value of ψ_a as follows:

$$\log \psi_a = \log \tau - \log \varepsilon + k \log at \tag{2}$$

"The need for the α-term means that the conception of firmness must include, as well as an estimate of the amount of deformation ..... another factor which depends on the extent to which a material is 'of a flowing nature'." This is closely related to the value of k for the materials selected. When the materials compared have k-values of ~ 0 (rubber) and 1 (bitumen) then the present experiment suggests that $a \sim {}^1/_3$.

Scott Blair & Coppen [1943] described further studies along similar lines, in which the complex synthetic material (see VIII, 2.1) was used for one of the comparison samples. The separate values of ψ for those samples which differ only quantitatively were denoted by ψ_m (the suffix m denoting a "multiple sample"). The corresponding value of ψ for the comparison standard was denoted by ψ_u (the suffix u denoting a "unique sample"). The values of k, determined experimentally, were denoted by k_u and k_m, and $k_u - k_m = \Delta k$. It was found that when p_u (the percentage of unique sample softer answers) was plotted against log $(\psi_m t_c^{\Delta k})$ a unique curve was obtained. Again a pronounced deviation was observed between the "point of subjective equality", defined by $p_u = 50$ and the point representing objective equality as defined by the *numerical* values of ψ_u and ψ_m (see Fig. 7).

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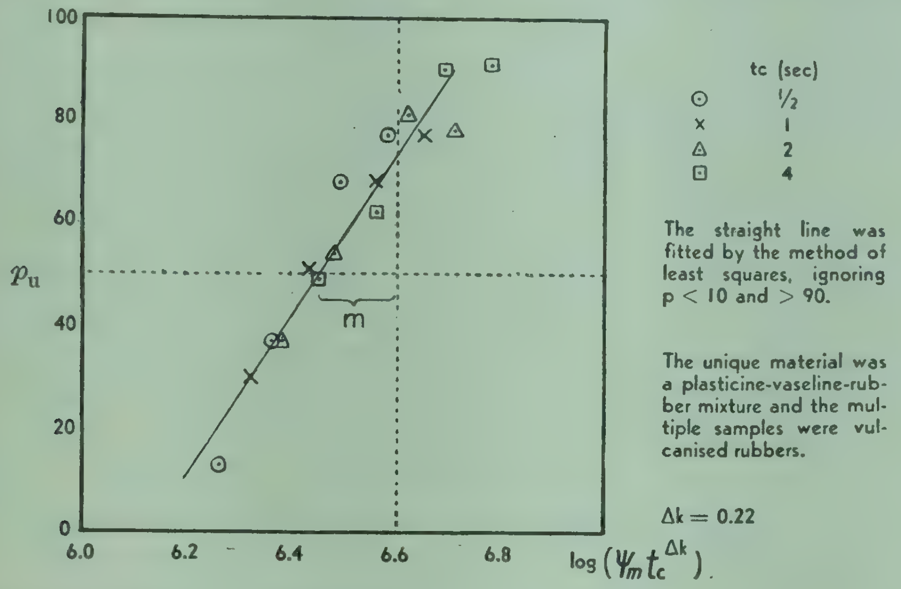
[1]) It was later stressed that the use of the α-term was no more than a simple algebraic device and that the meaning of the phenomenon might be better understood from the later approach (G.W.S.B.).



The straight line was fitted by the method of least squares, ignoring p < 10 and > 90.

The unique material was a plasticine-vaseline-rubber mixture and the multiple samples were vulcanised rubbers.

FIG. 7. Data from the simultaneous comparison of a number of rubber samples with a complex, synthetic sample.
[*from Scott Blair and Coppen, Amer. J. Psychol.* **56**, 234 (1943) p. 236].

Although at first sight it might appear to be a breach of dimensional homogeneity to indicate on the same figure both ψ_u and ψ_m, these are normally defined in terms of the objective unit of 1 sec. and inspection will show that $\psi_m t_c^{\Delta k}$ and ψ_u are dimensionally compatible and that for $t_c = 1$, $\psi_m t_c^{\Delta k}$ is numerically equal to ψ_m.

In the previous paper $\psi_m = G$ and $\psi_u = \eta$; $k_m = 0$, $k_u = 1$ consequently log $(\psi_m t_c^{\Delta k})$ corresponds to the previous abscissa of log (Gt_c). The former is, then, a more generalized treatment. The present paper included two experiments involving the comparison of several rubber samples with a selected bitumen (with replicates). The general numerical values of the elastic moduli and the viscosity were different, but the subjective adjustment factor (a) was found to be very similar (0.36 as opposed to 0.34). Further experiments were carried out in an attempt to assess the effect of "preconditioning" the subjects by requiring them to handle pairs of samples of rubber or bitumen before making the comparisons. Within the limits of the experimental technique (which cannot entirely rule out effects of learning and fatigue), the effects of conditioning were to reduce the deviation between the point of subjective equality and equality as objectively defined. If this deviation is denoted by m then m, a and Δk are related by the equation,

$$\log\, a = m/\Delta k \tag{3}$$

As a result of a number of experiments, not reported in detail, it was shown that the value of m is itself dependent upon Δk. When Δk is large (~ 1) then m is large, and m decreases with Δk until a value of about 0.4 is reached. Thereafter, m starts to increase again, although theoretically at least, it would be expected to return approximately to zero when $\Delta k = 0$ (i.e. when qualitatively similar materials are compared with one another). It is of interest to note that this secondary rise in the value of m occurs where there are relatively small qualitative differences, and that some of the subjects complained of the difficulty of doing the test with such small values of Δk. This observation is probably related to the discussion of heterogeneity (see VIII, 2.1).

Into this paper, the idea of using a *fractional derivative* of strain with respect to time as the physical criterion for the relative firmness of the samples concerned, was introduced. Such a process can be represented by means of the Γ function [1]), thus

$$\left|\frac{\overline{\partial^{\nu}\varepsilon}}{\partial t^{\nu}}\right. = \frac{\Gamma(k+1)}{\Gamma(k-\nu+1)} \cdot t^{k-\nu} \cdot \psi^{-1} \cdot \tau \tag{4}$$

assuming that equation 1 adequately covers the stress/strain/time relations of the material. Some of the points raised by this form of treatment will be dealt with later.

HARPER [1947] introduced more refined and satisfactory statistical treatment of some of the data contained in the two previous papers. This involved fitting an integral of the normal probability curve to the data expressed in the form of the proportion of judgments "unique sample softer" (p_{u}) against the physically defined differences $\log\,(\psi_{\mathrm{m}}\, t_c^{\Delta k})$. The essential constants are the median stimulus (or stimulus difference), usually measured as a deviation from the value of $\log\,(\psi_{\mathrm{u}})$ on the same figure, and the slope of the fitted curve which gives a measure of sensitivity of the discrimination. The presence of a significant deviation between the objectively defined equality and the subjectively assessed equality was shown to introduce a systematic bias into the chances of a specified difference being correctly detected.

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[1]) The symbol F represents fractional differentiation.

Further elaboration of the fractional differential treatment of the subjective aspects of the stress/strain/time relations was introduced, and it was shown that the value of the deviation between the point of subjective equality and objectively defined equality could be used to obtain a suitable value of the fractional exponent ν which would account for the observed deviation. At present, however, there is no means of assigning objectively the appropriate value of ν. This appears to be dependent not only on the separate properties of the materials compared, but also on the particular pair used. Fig. 8 shows various functions of strain for samples of rubber and bitumen whose modulus (G) and viscosity (η) are *numerically* equal. Included in this figure is the curve representing $\Big|\overline{\frac{d^{\nu}\varepsilon}{dt^{\nu}}}$ for $\nu = 0.66$, the value required to give a correct fit to the psychophysical data.

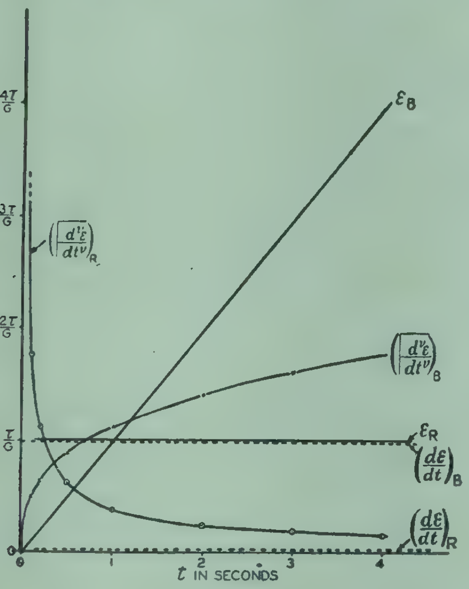

FIG. 8. Various functions of strain for the compression of rubber and bitumen samples. (Fractional derivative evaluated for $\nu = 0.66$).
[*from Harper, Amer. J. Psychol.* **60**, 554 (1947) p. 567].

In a later article (HARPER [1949b]) the technique of Probit Analysis was applied to the whole of the data obtained by Scott Blair and Coppen involving time-controlled comparison of qualitatively different materials. The constants obtained for each experiment were more precisely evaluated and expressions of the errors involved, included. The information derived is set out in Table 1 in which significant differences in the level of discrimination (b) and the median stimulus (m) are to be noted. In plotting the data the abscissa was modified to log $(\psi_m t_c^{\Delta k}/\psi_u)$, a dimensionless term (even before logarithms are taken). Very tentatively, graphs were prepared showing the values of b and m corresponding to specified values of k_u and k_m. For it was believed that b and m were related to k_u and k_m and not merely to their difference, Δk (see Fig. 9 and 10). It appeared that the values of b and the values of m (in the previous papers m was denoted by d) are not independent of one another so that it is probably premature

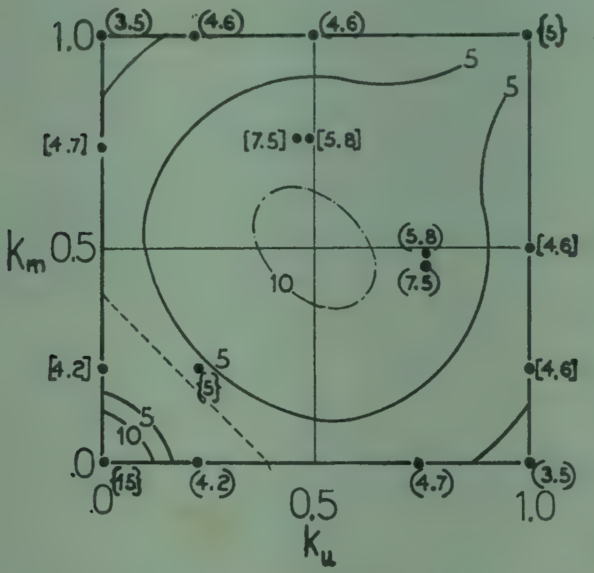

FIG. 9. Relationship between k_u, k_m and sensitivity of discrimination, *b*. [*from Harper, Amer. J. Psychol.* 62, 553 (1949) p. 556].

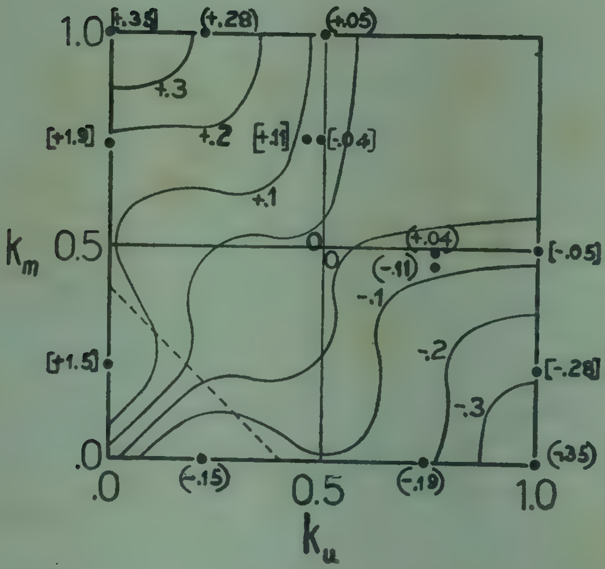

FIG. 10. Relationship between k_u, k_m and bias factor, *m*. [*from Harper, Amer. J. Psychol.* 62, 553 (1949) p. 557].

TABLE 1

[from Harper, *Amer. J. Psychol.* **62**, 554 (1949)]

Exper.	Materials compared		k_u	k_m	Δk	b	σ_b	m	σ_m	χ^2	$d.f.$	No. of replications	Group of subjects ¹)	Comments ²)
	Ψu	Ψm												
1	Bitumen	Rubber	1.00	0.00	+1.00	3.0	0.2	−0.35	0.02	20.2	14	40	A	
2	Bitumen	Rubber	1.00	0.00	+1.00	3.1	0.1	−0.46	0.01	72.4	14	160	A	
3	Bitumen	Rubber	1.00	0.00	+1.00	2.6	0.2	−0.34	0.07	24.4	14	40	B	Non-simultaneous comparison with one hand only.
4	Unv. Rubber	Bitumen	0.50	1.00	−0.50	4.6	0.3	+0.05	0.01	31.0	14	60	C	
5	Ersatz Cheese	Bitumen	0.22	1.00	−0.78	4.6	0.3	+0.28	0.01	39.6	14	58	D	
6	Ersatz Cheese	Rubber	0.22	0.00	+0.22	4.2	0.3	−0.15	0.01	15.2	14	60	E_1	
7	Non Newt. Bit.	Rubber	0.74	0.00	+0.74	4.7	0.3	−0.19	0.01	16.8	14	60	E_2	
8	Non Newt. Bit.	Raw rubber	0.76	0.47	+0.29	9.0	0.7	−0.08	0.01	15.4	6	60	E_3	Experiment 8 is subdivided into a and b as it appears that two distinct curves fit the data better than one. There were in fact *qualitative* differences in the two raw rubbers used.
8 (a)	Non Newt. Bit.	Raw rubber (R)	0.76	0.49	+0.27	5.8	1.7	+0.04	0.07	0.05	2	60	E_3	
8 (b)	Non Newt. Bit.	Raw rubber (G)	0.76	0.46*	+0.30	7.5	0.8	−0.11	0.01	0.48	2	60	E_3	
9	Bitumen	Rubber	1.00	0.00	+1.00	3.7	0.2	−0.45	0.01	27.5	14	60	E_4	Using a new level of stimuli.
10 (a)	Bitumen	Rubber	1.00	0.00	+1.00	3.9	0.2	−0.25	0.01	31.0	14	60	E_5	Preconditioned by handling bitumen only.
10 (b)	Bitumen	Rubber	1.00	0.00	+1.00	4.1	0.2	−0.31	0.01	48.5	14	60	E_6	Preconditioned by handling rubbers only.

¹) The use of the same symbol with a different suffix for a group of subjects denotes that only minor changes have occurred in its composition.

²) In comparing different experiments the changes in the group of subjects or practice, and boredom effects, amongst many others, may contribute to the observed changes. In the present form, adequate elimination of uncontrollable effects is difficult to secure.

b is a measure of sensitivity.

m is a measure of subjective bias.

to expect to be able to use the value of m to obtain a stable and invariant value of ν in the fractional differential expression given in equation (4) [1].

3. Investigations on Food Products

3. 1. *Bread and Dough*

KATZ [1937, 1938] made a systematic investigation into bakers' judgments of the properties of dough. Only a brief summary can be made here of the main points of this investigation, and reference to the original papers would be extremely profitable. Quite early in the report reference is made to the following comment by Scott Blair, "It seems to me that differences in certain physical properties are much more readily observed by "feel" than is the case with others. For example, we suspect that the hand is comparatively sensitive to changes in elastic modulus, but insensitive to changes of viscosity". This anticipated some of the later quantitative studies by Scott Blair and Coppen into the discrimination of differences in viscosity and elasticity, which have been reviewed above.

Katz points out the following essential problems:

(1) To analyze the exact meaning of the technical terms used by the bakers and to find out whether and to what extent these may be used for the scientific characterization of doughs.

(2) To analyze the baker's judgments psychologically. Which sense impressions form the basis of his judgments and how do the various senses cooperate? These questions cannot be answered simply by asking the baker for an analysis of his impressions, but only by observing the baker's response when the various conditions of handling the dough are changed. In addition, trained psychologists must be asked to describe and analyze their own sense impressions in handling the doughs.

(3) A first step is to find out whether the baker's judgments on the same dough on different occasions show good agreement, and then to see to what extent different bakers agree in describing the same dough. These tests can obviously be performed without leaving the subjective realm, but for this type of test only bakers of long experience and acknowledged reliability should be used.

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[1] One final remark on this form of treatment: HERMANS [1949] has indicated that the fractional differential approach is an alternative formulation of a more conventional mathematical treatment.

(4) Experiments also have to be carried out to determine to what extent the baker is successful in distinguishing various doughs, whose differences can be defined in an objective way. These experiments, he suggests, should lead to a clear decision as to whether the physicist's objective methods are superior to the baker's subjective ones.

It is important, from a psychological point of view, to distinguish the different ways in which the baker handles the dough because different groups of muscles and different sense organs, or at least muscles and sense organs in different combinations, are used on these various occasions. Two types of judgments are distinguished: an absolute judgment, such as "Very good body, tough, good spring, not short, immature". The object of the absolute judgment is to characterize a single flour or dough. The second type, the relative judgment, involves the comparison of two or more doughs. Examples of such relative judgments are "A more clay-like than B: B better ductility than C".

In describing dough Katz considers that the baker has certain specific sense impressions from which he *infers* properties of the dough which he cannot directly perceive. The most important characteristic of dough is what is termed "body". Body is considered to include four different properties which can be directly perceived.

(1) The degree of stickiness. A good body is characterized by a minimum stickiness.

(2) The degree of elasticity. Almost synonymous with elasticity are the terms spring, resilience, and firmness.

(3) The degree of toughness, which is judged when the dough is torn between two hands.

(4) The degree of extensibility or ductility. The opposite of ductility is shortness, a short dough breaking readily when it is stretched.

Visual judgments play an important part in the assessment of various doughs. If the baker has made the dough himself the different optical qualities of flour, such as the structure and macrostructure of the flour particles (size, shape etc.) and secondly the microstructure or the fine inner structure of the individual particles, give clues as to the precise origin of the flour. Experiments showed that a baker was not completely lost without vision and he could, if desired, rely solely on vision while another person manipulated the dough. Katz suggests that the sense of vision is likely to have been educated by the sense of touch.

Temperature of the dough also plays an important part in the general impression. The impression of temperature depends upon heat conduction, the actual temperature of the dough, specific heat, surface structure and intimacy of contact. Flour feels rather cool; cooler, for instance than wood. Dough feels cooler than the flour from which it is made, bread feels warmer than the dough.

In handling the dough only the fingers come into direct contact with it ¹). But, in addition to the sense of touch the sense organs of the muscles, sinews and joints in the hand, fore-arm, upper-arm and the shoulder are stimulated. With large masses of dough the muscles of the back also participate. The most important property which is perceived by the sense of touch is stickiness and the baker attempts to make his dough with the minimum degree of stickiness. Most of the properties which result in the stimulation of the sense organs of the skin, muscles and joints do so only if relative movement takes place. It is only thus that such properties as elasticity, toughness, and ductility are perceived. It is important to remember that the *physicist and the psychologist may require a different number of properties or even different properties, in order to provide a full description of the dough in their respective spheres* ²). It has long been known to the psychologist that the number of properties of the stimulus (e.g. of the dough), do not always correspond to the number of (psychological) properties of the corresponding sense impression. The psychological properties "body and spring" do not correspond to the physical properties viscosity and elasticity, but are rather the result of a complicated cooperation of the different senses of the skin, muscles, sinews and joints. HALTON & SCOTT BLAIR [1937] have indicated that the baker's impression of "spring" is closely related to the *ratio* of dough viscosity to its elasticity (i.e., the relaxation time). (See Chap. II, 2).

The experienced baker is not, of course, controlled exclusively by the sense impressions which he derives from handling a specific dough. The innumerable earlier experiences of similar doughs come in and contribute to the final judgment. If the baker knows or recognizes the origin of the flour he will expect certain properties in the dough made from it. Only too often, earlier experiences may act as prejudices.

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¹) Although this is Katz's observation, it would appear that the whole of the hand, especially "the heel of the hand" is employed.

²) Italics mine (R.H.)

Subjective impressions derived from manipulating the dough compare unfavourably in sensitivity with the objective methods of testing the dough properties. ¹) For instance, the addition of 30 % of Manitoba flour to English was only just detectable by subjective means, whereas it would be easily detected by instrumental means. The reliability of a baker's subjective judgments on dough is not great. For, although the judgments of the same baker on the same dough at different times showed good agreement, the judgments of different bakers on the same dough often show wide differences. Finally, a baker may not be very successful in judging various doughs whose differences (e.g. in elasticity or viscosity) can be defined in an objective way.

With regard to stickiness, however, differences in water content of 1 — 2 % could be detected (subjectively) between two otherwise identical doughs. It is therefore understandable why the baker places so much emphasis on this property. What he really does in making doughs is to produce a minimum of stickiness with a maximum water absorption. This is in agreement with the view of Halton and Scott Blair that, with the majority of flours, when the doughs have the required minimum degree of stickiness their other properties are also in a condition for giving satisfaction in the bakehouse.

A number of fundamental questions are raised by this and other investigations. Although these will be discussed in more detail in a later section, some comments are called for, at this stage. When the subjective judgment is compared with some form of objective measurement there are several independent questions involved. Assuming that the measurements are clearly defined, reliable and reproducible — an assumption which is not invariably justifiable in regard to rheological measurements on complex materials — then the effectiveness of the subjective judgment in responding to defined changes of the physical criterion may be assessed. However, it is very rare for the function of the subjective judgment to be merely that of assessing the physical condition of the material. Both instrumental measurements and subjective assessments are usually made in order to fulfil some additional function — the control of a manufacturing process,

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¹) A corresponding observation of the relative sensitivity of subjective judgments and objective measurements in connection with cheese grading is not invariably confirmed. (See HARPER & BARON [1950], also p. 233 below).

or the assessment of the probable consumer appeal of the finished product. That being so, the physical criterion cannot and must not be *assumed* to be more effective for these specific purposes than the skilled human judgment made under carefully controlled and standardized circumstances. No matter how *accurate* the physical data may be in themselves, the relative merits of the subjective and objective methods must be assessed in relation to their effectiveness in fulfilling their intended function, and the ease with which they may be carried out. This may be particularly important with materials which vary considerably from sample to sample. The number of replicate measurements or assessments required may be as important as the instrumental accuracy of any single member.

In assessing the performance of skilled workers it is essential to design methods which approximate closely to the normal conditions of working. Craftsmen are often very jealous of their skill and resent the intrusion of people who have come to "measure" them. Such an attitude may have the effect of lowering their apparent performance. The only way of overcoming these criticisms in some measure, is for a number of persons who are not seriously perturbed by being subjected to measurement to be trained over a considerable period and then studied experimentally. There would be no threat to the livelihood or the authority of the subjects of such an experimental study. This can hardly be said of investigations on the craftsman in industry, if he takes these studies at all seriously. It must be remembered that the "state of mind" of the subject, including his general attitude and motivation are part of the conditions of measurement in any psychophysical study.

3. 2. *Cheese and Butter*

Scott Blair, Coppen & Dearden [1941], included judgments of "firmness", as assessed by cheesemakers, bakers and others, in a study of the rheological properties of cheese. Six cheese [1] were used, controlled differences having been introduced into the manufacturing processes. Replicate cheese were subjected to detailed objective analyses. The cheese were placed in rank order of their measurements and assessments and comparisons were made. The most marked correspondence between the objective orders and the subjective assessments was found amongst the non-experts, then the bakers, and least correspondence was noted with the orders given by the cheesemakers. However, the objective tests were chosen, with few exceptions, on account of their correlation with *objectively* defined "firmness" and "springiness". It was suggested that the cheese experts found it impossible to dissociate judgment of firmness from other aspects known to be important in assessing quality.

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[1] Contrary to popular usage, the *technical* plural of "cheese" is "cheese" and not "cheeses".

SCOTT BLAIR, COPPEN & DEARDEN [1942] analyzed similar judgments made by cheesemakers, non-experts and routine chemical analysts. The subjects were required to place in order of "firmness" and subsequently in order of "spring" separate, small cubes cut from the experimental cheese. Many subjects expressed difficulty in assessing "spring", so these judgments were repeated by pressing the thumb on the outside of the whole cheese. In addition, the cheesemakers examined the cheese, scoring separately for body, texture, colour, taste and smell, and a composite grading score obtained. Although the cheesemakers showed wide discrepancies in the general score they showed a greater consistency, as individuals and as a group, in their assessment of "firmness" and "spring" compared with non-experts and routine chemical analysts. Two of the cheesemakers were unable to distinguish the respective orders for "firmness" and "spring", thus anticipating later observations by Baron and Harper (see V, 3). The present data concern solely self-consistency and do not involve a comparison with a physical criterion. Such a comparison leads to the following relationship, although the number rankings is too small to make more than tentative suggestions. The judgments of the experts on the sweet (low acid) cheese appear to agree more closely than those of the other two groups with measurements on the constant stress rheometer (see V, 3). Taste and smell gradings also correlate with the rheometer data. With the acid cheese, differences between the cheese were believed to be too small for accurate differentiation to be made. Individual differences as to what "spring" really involved were noted, and quite different orders were given, each tending to be correlated with a specific physical property. The Ball Compressor, which has been described in Chapter V, 3, seemed to give less useful information than the rheometer, being less accurate but easier to use without cutting the cheese. A complete parallelism was noted between an expert's grading on a set of 20 borings from factory made cheese and the objective "firmness" defined as the reciprocal of the total deformation using the Ball Compressor.

CAFFYN [1946] in an investigation mainly concerned with objective measurements on Cheshire Cheese (see V, 3 for this aspect of the data) observed that the total deformation on the bandaged cheese showed a remarkable agreement with the order of firmness as assessed by the grader. Of the few exceptions, most cases were those cheese which were high or low in the percentage of plastic deformation. Those with a high percentage of plastic deformation were "down graded" (i.e. judged to be softer than would have otherwise been expected), and vice versa. This observation confirms later experimental evidence of the complex nature of the physical behaviour underlying judgments of firmness. Caffyn's view that, providing an adequate number of repeated measurements are obtained, the Ball Compressor is more sensitive than the thumb requires considerable qualification. When comparisons are made between the objective measurements and the subjective judgments under comparable conditions, then for the more skilled assessors the subjective judgment may *not* be inferior to the objective measurements (see HARPER & BARON [1950], outlined in V, 3).

BARON [1947] observed that the grader's judgments on 58 Cheshire Cheese were correlated with the objective measurements. The firmness judgment was correlated with the Ball Compressor total deformation (B.C.T.) and, to a less extent, with the Ball Compressor percentage plastic deformation (B.C. % P.) The grader's judgments of quality, although related to the B.C.T., were more clearly related to the Borer measurements [1]). (See chapter V). BARON [1949a, b] confirmed, from another small sample of cheese (28), that an expert's judgments of "body" were in almost complete agreement with instrumental measurements. In studying the ripening of Cheshire Cheese, BARON [1949c] indicated that selected members of two groups of cheese, one badly tainted, soft, mushy and lacking in body, the other without serious criticism, could be distinguished rheologically throughout the ripening process. Further aspects of these and subsequent investigations are contained in the section devoted to Factor Analysis (see VIII, 4, 3).

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[1]) The Borer consisted of a cylindrical cork borer which was loaded and allowed to penetrate the cheese. The amount of penetration at any instant was observed by reading an attached vernier.

Mocquot, Scott Blair & Baron [1947] included some interesting observations on subjective judgments on Gruyère cheese and the relationship between these judgments and rheological measurements. One of the advantages of the Ball Compressor as a method of assessing firmness is that cheese of different temperatures may be compared. "A cheese expert, even if he has had long practice in his profession, is not always capable of making such a comparison and therefore finds himself deprived of an important factor in judgment."

Commenting on the value of the Ball Compressor measurements in predicting "quality", the authors state that tests carried out on several batches of cheese made in various factories show that it is difficult to lay down general limits of deformation, above and below which the cheese would be too hard or too soft, or of good or bad flavour. On the other hand for batches made under similar conditions during several months there is a fair correspondence between the tests made at one stage and the final gradings carried out about a month later. Correlations of 0.78, 0.74 and 0.63 were obtained between the grader's marks and Ball Compressor total deformation, Ball Compressor plastic deformation and the percent plastic, respectively.

Harper & Baron [1949] outlined the subjective aspects of the relationship between the mechanical properties of Cheshire Cheese and its quality, assessed subjectively. The study extended over a period of 2½ months and, in addition to the general measurement programme, each of about 200 cheese were rated on a five or a seven point scale. Ratings for firmness and springiness were made on the outside of the cheese, ratings for firmness, springiness, crumbliness and overall quality were made on the plug taken with a cheesemaker's sampling iron. Comments on flavour and any other striking characteristics were recorded. In part of the experiment four individuals expressed their views, in another part, only three. Only the assessments on the two months old cheese were discussed. Marked individual differences were noted. On the same group of cheese one individual made adverse criticism of three times as many cheese as did the other two judges. Fig. 11 indicates the differences between individuals in their average rating of the separate batches of cheese for firmness and overall quality. On the average, the cheesemaker (A) considered the cheese to be 1.1 points better in quality (on a seven point scale) than the other persons considered them to be. Some differences are in evidence in the judgments of firmness. Individual B appears to show

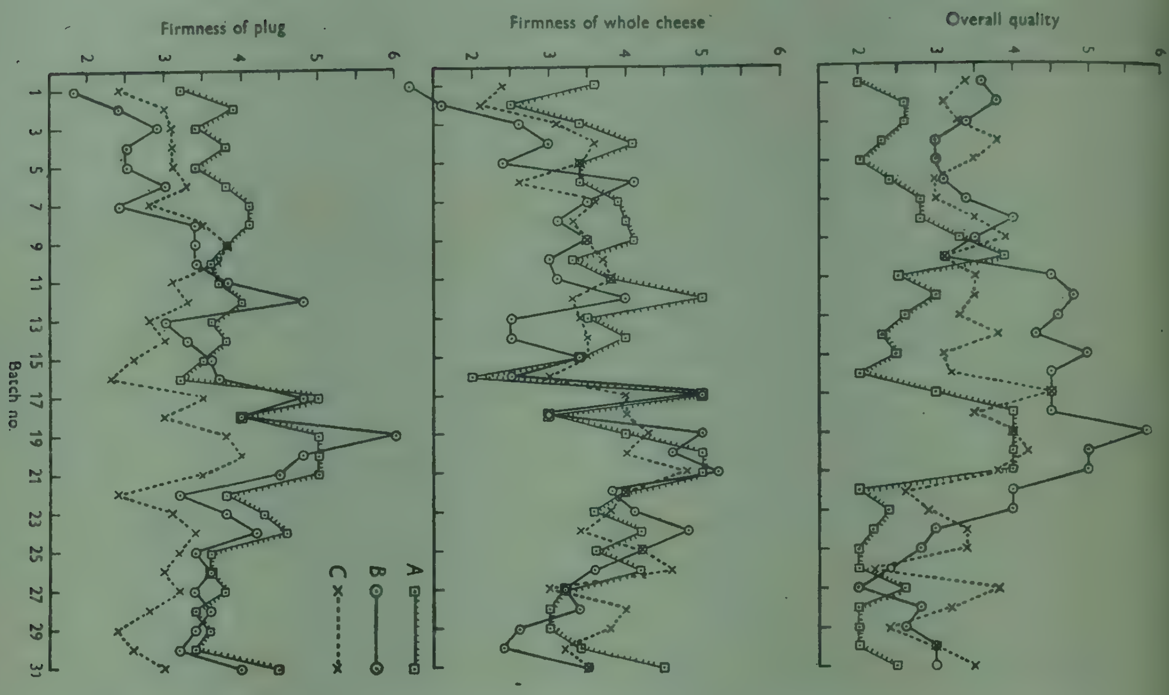

FIG. 11. Mean ratings of successive batches of cheese by three individuals A, B and C.
[*from Harper and Baron, J. Dairy Res.* **16,** 363 (1949) p. 365].

a progressive drift in rating firmness, relative to the other two, as the experiment progressed. This has been interpreted, tentatively, as due to the change-over from previously rating the objectively softer, two weeks old cheese. That a similar trend was not observed in the assessments of the other two individuals may have been due to their experience — A being a professional cheesemaker and C having carried out many experiments on judging the firmness of vulcanized rubber (see VIII, 2.1). The average relationship between the various assessments and measurements are shown in Fig. 12. It was suggested that the firmness rating on the two weeks old cheese or a measurement with the Ball Compressor might be used to "screen off" the greater proportion of cheese which ultimately develop unsatisfactorily. The actual technique and "cut off level" would have to be developed separately for each factory.

HARPER & BARON [1950] made a systematic study of the replicate judgments of a number of individuals on selected groups of cheese. Included in this were the judgments of a professional grader of long standing and experience. The cheese assessed in two separate experi-

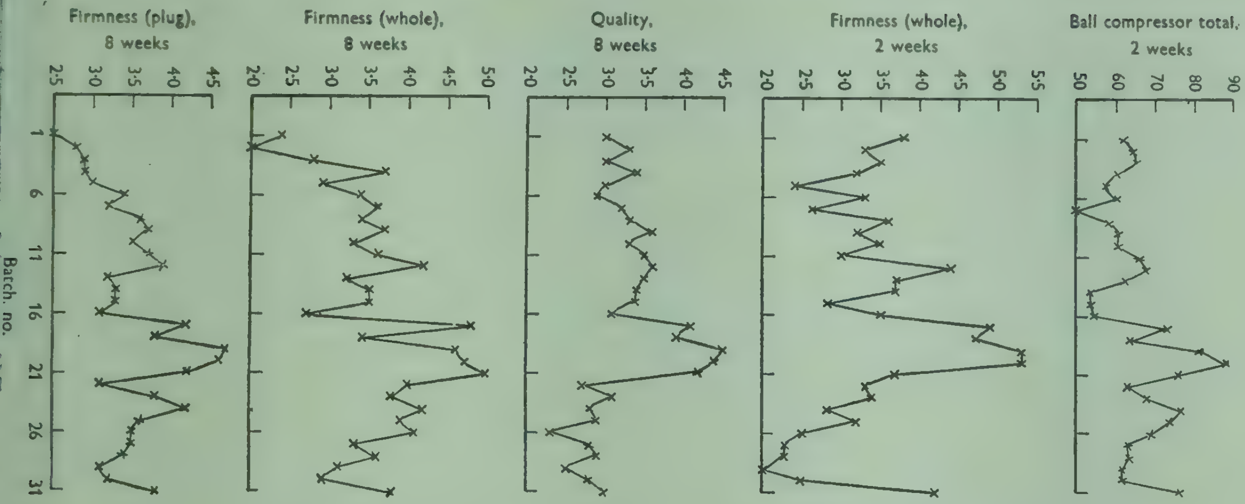

FIG. 12. Average measurements or ratings on successive batches of cheese. [*from Harper and Baron, J. Dairy Res.* **16**, 363. (1949) p. 366].

ments were: (1) A group which although believed to differ detectably contained no cheese which were seriously defective, and (2) A group of cheese covering a wider range of variation. In assessing the first group the professional grader frequently showed perfect consistency but no differentiation. When forced to differentiate by the degree of the differences, the grader's judgment, as expressed in this form, was generally less effective than the other members of the team. In assessing the rheological characteristics which have been termed "firmness" the professional grader rarely made any attempt at differentiating between the cheese. His method of pressing lightly on the surface did not facilitate such differentiation. However, the mere absence of differentiation does not necessarily mean that he would find it impossible to do so by "thumbing" or by the use of auxiliary clues. The most effective discrimination was found in the individual who was concerned with organizing the objective testing programme and who knew that only by differentiating maximally could the relations between the various assessments and measurements be established satisfactorily. One might say that this individual was "looking for differences", again stressing the part played by mental attitude in sensory judgments. It is of special interest to note that this individual showed herself to be more effective in her discrimination than the instrumental measurements.

In this field, systematic work on butter seems to be extremely scanty, although, as indicated later, a programme of research into the rheological properties of butter margarine and cooking fats is in process of development. Ultimately this too may include studies of the relationship between subjective assessments and objective measurements. KRUISHEER *et al.* [1938] have observed that butter undergoes permanent deformation only at pressures exceeding a certain limit. Deriving a "yield-value" by graphical methods from the data obtained by means of a simple plastometer (see Chap. IV) he showed a close parallelism between the yield value of several samples of butter and the points given to these samples for firmness by experienced graders. He therefore proposed to replace the hitherto undefined "firmness" of the butter by the calculated "yield-value". A simple hand apparatus was designed, but gave indications that systematic differences due to the method of application might occur. A mechanically driven apparatus was designed to eliminate this personal factor. Both instruments gave measurements closely related to the points given in normal grading practice. Whether the small deviations between the subjective assessment of firmness and the measured "yield-values" might be accounted for by other aspects of the objective behaviour of the butter under test cannot be answered from the data available.

4. Factor Analysis and the Rheology of Foodstuffs

4. 1. *The Purpose of Factor Analysis*

In this part, the statistical technique known to mathematical psychologists as "Factor Analysis" and its application to the study of the rheology of foodstuffs will be outlined. One function of this technique is to reduce extensive groups of more or less empirical test data into a convenient and compact form. After some initial training, this enables the investigator to see at a glance the main relationships and, occasionally, to identify or to define some of the underlying "properties". The method has been developed in an attempt to reduce to order the complex relations between a variety of mental tests which might be given to a group of individuals. The computational techniques will not be described in detail nor can all the steps involved in interpreting a study along these lines be covered. As a statistical method, Factor Analysis has not yet passed beyond the controversial stage. However, suggestions will be made as to the nature of the uncertainties involved, as they arise. The writer is convinced that, in spite of its imperfections, Factor Analysis does supply information not readily obtainable from other statistical techniques.

4. 2. *The Algebraic Relationships involved in Factor Analysis*

The fundamentals of the procedure are as follows. The correlation coefficients [1]) between the various sets of measurements are calculated and set out in the form of a square table or matrix leaving the diagonal cells black, since entries in these are not part of the experimentally determined data.

Matrix of Correlations

Test	a	b	c	d	. . .
Test					
a	—				
b	$r_{\rm ab}$	—			
c	$r_{\rm ac}$	$r_{\rm bc}$	—		
d	$r_{\rm ad}$	$r_{\rm bd}$	$r_{\rm cd}$	—	
. . .	. . .	. . .	. . .	. . .	. . .

The aim of the analysis is to calculate a set of numerical "loadings" for each test in a number of independent, postulated "factors" less numerous than the tests.

Factor Matrix

Factor . .	I	II	III
Test			
a	a_1	a_2	a_3
b	b_1	b_2	b_3
c	c_1	c_2	c_3
d	d_1	d_2	d_3
. . .	. . .	. . .	. . .

such that any of the original correlation coefficients may be reconstructed according to the following equation, assuming only three factors.

$$r_{\rm ab} = a_1b_1 + a_2b_2 + a_3b_3 \tag{1}$$

There are in existence several slightly different techniques which represent different approximations by means of computational short cuts to the same final solution, the most stable of which would be that minimizing the sum of the squares of the deviations between the original correlations and their reconstructed values. If the analysis is to be made in terms of the minimum number of "*common factors*" then the

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[1]) The correlation between two sets of test measurements, represented by the following expression:

$$r_{xy} = \frac{\sum(x-\bar{x})\,(y-\bar{y})}{\{\sum(x-\bar{x})^2 \cdot \sum(y-\bar{y})^2\}^{1/2}}$$

in which $\bar{x}$ and $\bar{y}$ are the means of the values of x and y.

appropriate entry in the diagonal cell is the "*communality*". The "communality" is normally less than unity, and represents the proportion of the variance in a given test common to others. Since the diagonal cells are symbolized by terms of the type r_{aa} it might have been expected that the self correlations should have been inserted and that these would have been equal to unity. However, if these were determined experimentally by a test-retest correlation, then errors of measurement would have reduced these values to something less than unity. The existence of factors not common to other tests reduces the required value still further since such "specific factors", as they are termed, play no part in the rest of the correlation matrix. The "communality" is equal to the sum of the squares of the factor loadings and is normally designated by h^2. It can be shown that the appropriate value of h^2 for each test is given by an equation of the type:

$$h_a^2 = a_1^2 + a_2^2 + a_3^2 \tag{2}$$

The actual value of h^2 has to be estimated in the first instance and the value may be improved by a process of successive approximation. Analysis may also be made in such a manner as to account for the whole of the variance 1) of the test measurements by using entries of unity in the diagonal cells, but this solution is often more difficult to interpret since it involves factors which contribute only to the diagonal entries. Since these are not "common factors", they are of restricted interest.

In general, the analysis in terms of the smallest number of common factors permits the most effective reconstruction of the correlations to be made, whereas the analysis with unities in the diagonal cells is more effective where the prediction or reconstruction of the test measurements is concerned. Only the analysis in terms of common factors will be discussed here.

The graphical representation of factors

In order to make graphical representation of factorial relationships it is useful to consider simplified cases restricted to two common factors. The case for three common factors may be dealt with by means of three dimensional models, but beyond this recourse has to be

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1) The variance of a set of N measurements is simply $\Sigma(x-\bar{x})^2/(N-1)$ and indicates the extent of the variation between the individual measurements about the mean $\bar{x}$; the square root of the variance is termed the standard deviation.

made to formal mathematics. Matrix algebra is the ideal medium for expressing factorial relationship in the present development of the techniques.

Let us consider, then, the ideal condition in which two tests, a and b, have been analyzed *completely* into two orthogonal factors.

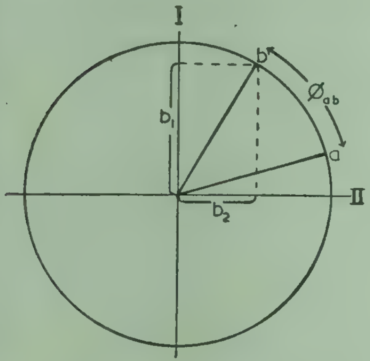

FIG. 13. Representation of the relation between two ideal tests a and b assumed to involve only two common factors.

In such a case the tests may be represented by two points on the circumference of a unit circle [1]), and the "factor loadings" are represented by the projections of the radius vector on to the axes I and II. It can readily be shown that the correlation between the two tests is equal to the cosine of the angle ϕ_{ab} between the two "test vectors". Where there are only two common factors and these are inadequate to account for the entire distribution of test measurements (variance) the points a and b lie within the same circle at distances h_a and h_b from the origin. The factor loadings are still the projection of the test vectors upon the two orthogonal factor axes, but the test vectors of unit length now no longer lie in the plane of the factor axes. The cosine of the *space angle* between the test vectors still represents the correlation between the tests, or if ϕ_{ab} is the angle on the two dimensional projection,

$$r_{ab} = h_a h_b \cos \phi_{ab}$$

Even from the two dimensional diagram, it is evident that, since the data determine only the angles between the test vectors, the relationships between the tests (i.e. their intercorrelations) may equally well be represented by any pair of "factor axes" so long as these remain in the original plane containing I and II. In fact there is an infinite number of sets of orthogonal axes which would satisfy the required conditions. One of the most difficult and controversial operations of factor analysis is that of selecting the most effective set of axes for describing the relationship between tests. The original set is primarily determined by the accident of selecting a particular group of tests and materials for analysis. The first set is extracted in such a way that each factor in turn accounts for the maximum amount of test variance. Some writers prefer to retain the original solution for interpretation: others prefer to "rotate" the original set of axes into a new position determined by additional criteria. One criterion is to maximize the number of zero loadings: another is to allow the axes to take up positions related to the structure shown by the points representing the ends of the test vectors, in what is normally termed the "common factor space". Whatever method is used, the final set of factors is interpreted in relation to the pattern of factor loadings and the qualitative nature of the tests, where this is known.

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[1]) The unit radius represents the standardized value of the square root of the total variance of each test.

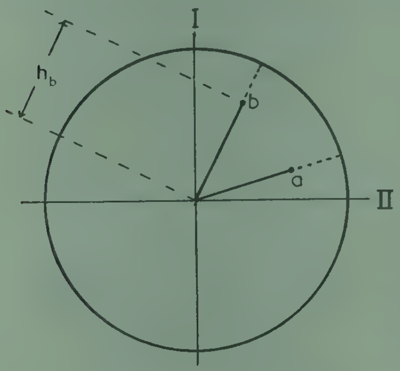

Fig. 14. Representation of the relation between two tests a and b, subject to error or specific variance, and assumed to involve only two common factors.

There is no *a priori* reason why the factors themselves should not be permitted to depart from the original condition of independence or orthogonality. Under certain circumstances *oblique* solutions may be desirable, particularly where practical restrictions occur in the values which the measurements in the various tests may take. THURSTONE [1947] has become thoroughly convinced of the value of oblique factors. It should be noted that "factors" can only be isolated by the present techniques in so far as they (the factors) contribute to difference between the measurements on the different samples. Thus, if by selection, variations due to a particular factor are eliminated in a given set of samples tested, then the factor concerned cannot be isolated by the present methods.

It is reasonable to enquire, "What are factors?" In general, they seem to represent useful principles of classification by means of which the phenomena observed may conveniently be described. In addition, *some* factors may be thought of as ideal tests which may be designed or approximated to by the statistical combination of several existing tests. The factor loadings represent the intercorrelation between these ideal tests and the real tests. Not necessarily all factors will be found to correspond to physical properties of materials, as usually defined, in instances where the tests investigate the behaviour of materials. The principles of classification corresponding to the factors which may be extracted from the analysis of rheological tests may represent the number of independent ways in which the behaviour of a material may vary, such as "hardness", "springiness", "hardening", etc., but if larger batteries of tests are used, including electrical tests and other tests of fundamental properties, a link may be found between the phenomenological or descriptive approach and the analytical approach to the problems involved.

As developed at present, factor analysis is restricted to the assumption of linear relationships between tests. Where relations are known to be non-linear, some loss of information may be incurred. Where relationships are complex the assumption of linearity, as a first approximation, may be a first step towards unravelling some of the problems which confront many of us in the form of a mass of test data too extensive to permit assimilation and understanding.

Caution is necessary in generalizing the results of a factorial study 1) obtained from one set of tests and materials to another set selected, overtly or not, on a different basis. Strictly speaking, there is no short cut to the information to be derived from a *series* of *planned* factorial studies, for factors only have meaning in so far as they remain stable and identifiable under different circumstances. The numerical loadings may change, due to selection, but the pattern should remain much the same. In spite of this restriction, valuable information may be forthcoming even from preliminary studies as to the complexity of the behaviour measured, the relationship between the tests and the qualitative nature of some of them. This may turn out to be con-

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1) In the present context, the term "factorial" study will be used to denote the phrase "a study employing the technique of Factor Analysis", as outlined in the present section. This should not be confused with use of the term "factorial design" which generally implies statistical planning using a number of strictly orthogonal and statistically independent *treatments* in an experiment. Factor Analysis has been developed in an attempt to deal with the problems of a set of non-independent variables.

siderably different from what was originally intended. Factorial studies lead to modifications in the tests or instruments used and to the rejection of some as merely duplicating what is obtained by other means. This in turn leads to further studies and to the formulation of hypotheses which may be tested experimentally. Some writers believe that factor analysis can only be used to test hypotheses which have been used in the design of a factorial study. Others believe that hypotheses may themselves be formulated from the results of a factorial study ¹).

4. 3. *Experimental Investigations*

The first attempt to utilize Factor Analysis in this complex field was a study by HARPER & BARON [1948] of the relations between a number of empirical tests on Cheddar Cheese. The data had been obtained in the course of a routine, field investigation, which had not been specifically planned with a view to using Factor Analysis. Previously, the correlations had been tabulated together with various orders of partial correlation, but high order partial correlations are extremely difficult to interpret. The observed correlations could be reproduced by means of three independent "factors", the third factor probably being only just significant. Analysis of the pattern of the loadings in relation to the specific tests suggested that the first factor was closely related to "hardness" (being correlated to the extent of .96 with a ball indentation test) which might be used to *define* this factor, the second factor was related to "springiness" and the third, very tentatively, to "hardening".

Among the interesting features of this analysis was the observation that a test originally designed to assess "hardening" — a form of Meyer analysis — was found to be linked (in a negative sense) with the *recovery* of the material tested. Modifications in the design of this instrument were therefore made.

The previous study ¹) and the experience gained in carrying it out were used to plan a more systematic experiment in which subjective

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¹) *General References.*
BURT, C., Factors of the Mind.
THOMSON, G. H., The Factorial Analysis of Human Abilities.
HOLTZINGER, H. J. & HARMAN, H. H., Factor Analysis.
THURSTONE, L. L., Multiple Factor Analysis.
WOLFLE, D., Factor Analysis to 1940.

assessments on the essential characteristics of the cheese were included, in addition to a more comprehensive set of objective (instrumental) tests. (BARON & HARPER [1950]). The tests have been described elsewhere (see Chap. V). The subjective assessments took the form of ratings on a five or a seven point scale and were averaged for the group of judges (3 in number). On the overall quality scale 1 represented "excellent", 4 "average" and 7 "very poor", while on the firmness scale 1 denoted "very firm", 4 "average" and 7 "very soft". The measurements and mean ratings in each test were correlated and Factor Analysis applied to the set of correlations. The main conclusions from this investigation were:

(1) Four "factors" or independent sources of variation were required to account for the observed relations between the tests.

(2) There was no evidence to suggest that the information derived from the subjective tests was qualitatively different from that obtained objectively.

(3) The first factor (unrotated) accounted for 47 % of the total variance. The pattern of the factor loadings suggested that this factor was closely related to the cohesion of the material, such as might be expected to be included under the grader's term "body".

(4) Some of the tests were carried out through the rind of the cheese and some within the cheese, the effects of the rind having thus been removed. These two distinct groupings of the conditions of testing were believed to have contributed to the second factor.

(5) Springiness and firmness, as assessed subjectively on the outside of the cheese, appeared to be indistinguishable in factorial composition. This is of special interest, for the cheesemaker refused to give separate evaluations of these two items (cf. VIII, 3.2).

(6) The third factor was interpreted as indicating that "springiness" has to be taken into account in describing both the tests and the cheese, although it was impossible to state, categorically, whether it is the *rate* or the *amount* of springiness which should be included in the term.

(7) The fourth factor seemed to be related to the influence of the duration of the tests on the observed measurements. Its total contribution was small and this interpretation is very tentative.

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1) The same method was used by HARPER, KENT & SCOTT BLAIR [1950] to test the method, incidentally demonstrating the relationship between a number of electrical and rheological tests on plastics.

In essence, the conclusions from a preliminary study by means of Factor Analysis are hypotheses to be tested by subsequent studies. The *identification* of factors may be a tentative process and the rules for such interpretation are by no means finally developed. However, if a test can be found which correlates to the extent of unity (or nearly unity) with a given factor it may be convenient to use this test for descriptive purposes. Identity and correspondence are not precisely the same, although it may be impossible to distinguish these two conditions within a single study. Perhaps the most valuable functions of Factor Analysis in the present studies have been:

(1) To arrange tests into groups representing those which place the materials tested in a similar order of measurements.

(2) To determine the minimum number of independent ways in which the material tested may vary and to select the most suitable and efficient tests for purposes of description.

(3) Once a particular standard "battery" of tests has been selected, the qualitative nature of new empirical tests may be assessed by analyzing these along with the selected standards.

No new factorial study is complete in isolation, but usually represents the first of a series, each of which may contribute to a fuller understanding of the relationships between the tests. Also, relative to a framework which has first to be created, it may help to reveal the nature of other complex, empirical tests.

Further studies along these lines are still in progress. HARPER & BARON [1951] have recently reported a more extensive study, along similar lines, on samples of cheese from the continuous output of a commercial cheese factory. Although the actual numerical values of the correlation coefficients and factor loadings are not identical with those of the previous study, a considerable measure of agreement is shown. This is effectively indicated by a direct comparison of three dimensional models representing the three main factors in the successive investigations. Another aspect of the later study has been the addition of four new tests into the analysis, thus providing information as to their nature in relation to an established background.

Another investigation which may be assisted by the use of factor analysis is a study of the "spreadability" and other essential properties of butter, margarine and cooking fats. Empirical tests are being built up and it is proposed ultimately, to test a large number of samples of each material and to analyze the correlations between the tests.

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